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VOLUME II:

KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
PANEL PRESENTATIONS
LIQUID & SOLID WASTE RESEARCH
ANALYTICAL METHODS RESEARCH
ENVIRONMENTAL SOCIO-
ECONOMICS RESEARCH
MULTIMEDIA CONTAMINANTS &
BIOTECHNOLOGY RESEARCH

THE CHALLENGES OF A NEW DECADE

November 19 & 20, 1990
Royal York Hotel
Toronto, Ontario
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Sponsored by

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Environment Ontario

Ontario, Canada

Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1990 Technology Transfer Conference are published in two volumes of conference Proceedings corresponding to the following sessions:

VOLUME I: KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
PANEL PRESENTATIONS
AIR QUALITY RESEARCH
WATER QUALITY RESEARCH

VOLUME II: KEYNOTE PRESENTATIONS
FEATURE PRESENTATIONS
PANEL PRESENTATIONS
LIQUID & SOLID WASTE RESEARCH
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MULTIMEDIA CONTAMINANTS &
BIOTECHNOLOGY

Volume II is comprised of presentations given during Session C, Session D, Session E and Session C of the conference, as well as all Keynote, Feature, and Panel Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4574 or 323-4573

Acknowledgments

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The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of Environment Ontario, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Keynote Paper I

Sustainable Development: The Technological Challenge
Noel J. Brown, Director, United Nations Environment
Programme, North America

PAPER NOT AVAILABLE AT TIME OF PRINT

"RESPONSES TO GLOBAL CHANGE:

the Coming Environmental and Economic Revolutions"

Keynote address: J. P. Bruce

Environmental Research: Technology Transfer Conference
Toronto, 19-20 November 1990

Extended Abstract:

The Intergovernmental Panel on Climate Change has provided in 1990, the most definitive scientific assessment to date of the changes in greenhouse gas concentrations in the atmosphere and the probable effects on the world's climate. This consensus report of more than 300 scientists from many countries, places the major conclusions in 4 main categories of descending degrees of scientific certainty. The Panel is certain that in the atmosphere and that human activities are substantially increasing greenhouse gas concentrations in the atmosphere and that the natural radiation exchanges known as the "greenhouse effect", are real. They "calculate with confidence" that CO₂ has caused and will continue to produce more than half of the human-enhanced greenhouse effect, and that the long-lived gases, (CO₂, nitrous oxides and the CFC's) would require immediate emission reductions of more than 60% to stabilize atmospheric concentrations at present levels. They predict, based on current model results, that if nothing is done, i.e. a "business-as-usual" scenario prevails, global mean temperatures will rise 0.3 degrees C per decade (with a range of 0.2 to 0.5 degrees C) and sea level will rise 6 cm per decade (range 3-10cm) over the next century. These are rates greater than ever experienced since man first tilled the soil, some 10,000 years ago. Northern latitudes and large land areas, like central and northern North America, are predicted to warm more rapidly than the global mean. The impacts of such changes on coastal communities, small islands, water resources, agriculture, forestry, the spread of tropical diseases, would be increasingly profound over the next 100 years. At their lowest level of certainty, they advise that their judgement is that the mean global temperature has already risen 0.3 degrees to 0.6 degrees C over the past 100 years, "broadly consistent with predictions of climate models".

Responses to this prospect have, on the one hand, been widespread alarm, especially on the part of low lying island countries and ones with extensive low coastlines, and countries with only marginal agriculture and water resources. Spokesmen for other countries, such as USSR, see a somewhat warmer climate as mostly advantageous. A number of western European countries, and scattered sub-national jurisdictions elsewhere have already announced plans to cut CO2 emissions, and some, including Canada, have committed themselves to a stabilization of emissions.

However, most agree that concentrated, coordinated international actions are needed to really reduce the rate of accumulation of greenhouse gases and attention is now focussed on negotiation of a global convention on climate change, hopefully by the item of the UN Conference on Environment and Development in Brazil, June 1992. The urgency is great, since as the IPCC points out, if nations can cut CO2 emissions by 2% per annum beginning in 1990, concentrations will be stabilized at 390 parts per million by 2020 or so, but if cuts are delayed 20 years, stabilization will not occur until 2070, and then at a much higher 460 ppm.

There are four major contentious issues which will have to be resolved in negotiations of a Convention on Climate Change. These are:

- 1) a plan to cut greenhouse gas emissions, especially CO2;
- 2) a plan to move from net global deforestation to afforestation;
- 3) transfer of funds or other economic incentives to permit developing countries to make the necessary investments and adjustments, and
- 4) transfer to developing countries on a preferred basis, of low emission technologies.

All of these issues have potentially enormous economic as well as environmental implications.

The first will require, above all, a major change in energy policies of the nations, especially the highest per capita energy users, Canada and USA. The key requirements are aggressive conservation strategies driven by end-use oriented services rather than the supply side, and switching to lower CO2 emitting fuels, away from oil and coal. Examples of what is achievable at low net cost in North America and India will be outlined.

In the business world, our major industrial competitors, in Europe and Japan, are already much more energy efficient than North America, and are adopting even greater efficiency measures. There is every reason to fear for the future competitiveness of Canada and USA if energy efficiency is not pursued vigorously in the next few decades.

The third of these issues is one stressed by developing countries in all of the pre-negotiation meetings. Without major initial financial investments, they will be unable to institute the energy efficiency, fuel switching and reforestation measures needed to prevent them from augmenting greenhouse gas emissions at a rapid rate to meet the increasing needs and expectations of their people. Such investments are clearly impossible in a world in which the net financial flow is away from the developing world with low commodity prices and huge debts, to the industrialized countries. This flow must be reversed, or at a minimum a major fund, greatly exceeding the \$270 million committed to a CFC replacement fund, will be required to permit the developing countries to be full partners in a world-wide effort to protect the global atmosphere.

The recent success of the world community, in agreeing to a strengthened plan for CFC emission controls to protect the ozone layer under the Montreal protocol lends some optimism to the prospect of a more comprehensive climate change convention. It also buys a little time through CFC reductions to put in place the more difficult CO₂, methane and nitrous oxide controls.

However, the major issues on the table can only be resolved if the industrialized countries accept their responsibility to greatly reduce their own greenhouse gas emissions, increase afforestation, and assist developing countries to do the same. Revolutions in our thinking about, and use of, energy, and in our relationships with developing countries are urgently needed if we are to protect the atmosphere of our small planet and the climate it produces.

VOLUME II
FEATURE PRESENTATIONS

WHAT'S THE LATEST ON ACID DEPOSITION IN NORTH AMERICA?

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This presentation summarizes the results of the National Acid Precipitation Assessment Program State of Science/Technology Report Deposition Monitoring: Methods and Results (Sisterson et al. 1990). The larger document discusses methods to monitor wet, dry, and droplet deposition in the United States and Canada and provides temporal and spatial analyses for the period 1979-1987. A significant portion of the document addresses the representativeness and completeness of large-scale network deposition data at regional and local scales.

The most complete deposition monitoring results are for wet deposition. Information on dry deposition is insufficient to allow spatial and temporal analyses on a regional scale of the major acidic deposition species and their precursors. Information on droplet deposition (i.e., deposition by interception of cloud water and fog droplets, sometimes called "occult" deposition) is even more recent than that on dry deposition, and little information exists for spatial and temporal analyses except at a few sites.

The areas of maximum wet deposition of individual inorganic chemical species in precipitation are located in the northeastern United States and southeastern Canada, and those locations have not changed significantly in the past decade. The weight of scientific evidence suggests that all analytes except pH or acidity exhibited a decreasing (not statistically significant) trend in deposition and concentration in 1979-1987 for the eastern half of the United States and Canada. Median annual precipitation-weighted concentrations are larger in North America than in remote regions of the world by factors of 9 for SO_4^{2-} , 14 for NO_3^- , 7 for NH_4^+ , and 4 for H^+ . The average pH of precipitation in remote regions of the world is closer to 5.0 than to 5.6. Excluding precipitation monitoring sites from urban areas and the influence of major local sources causes the integrated wet deposition chemistry estimates to be low.

The finding that sulfur and nitrogen species in precipitation have decreased but pH has not changed is perhaps the single largest surprise of the State of Science Report. A large decrease in calcium and other base cations offsets decreases in acid species in precipitation. The reason for the decrease in calcium is not clear. In part, it can be attributed to changes in agricultural practices, paving of rural gravel highways, and perhaps emission controls; the same emission controls that remove sulfur and

nitrogen species from smokestacks may also remove base cations such as calcium that reduce precipitation acidity.

Preliminary results indicate that dry deposition for sulfur is between 0.3 and 0.5 of the wet plus dry deposition at regionally representative sites and is between 0.3 and 0.7 for nitrogen. Most of the dry-deposited sulfur is due to SO_2 , with values of 50-90%. Most of the dry-deposited nitrogen is due to HNO_3 , with values of 76-88%. The ratio of dry plus wet deposition of sulfur species to that of nitrogen species varies between 4.25 and 0.77.

Concentrations of H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ are 5-20 times larger in cloud water at high-elevation sites than in precipitation. Droplet deposition of H^+ , SO_4^{2-} , NO_3^- , and NH_4^+ is up to three times wet plus dry deposition in the warm season for high-elevation sites that are frequently in cloud. High-elevation sites above 600 m experienced in-cloud conditions 30-40% of the time during the growing season (April-October). The liquid water content averaged about 0.20 g m^{-3} at most sites.

By using these wet, dry, and droplet deposition data together with anthropogenic emissions and an estimated urban perturbation factor for wet and dry deposition, S and $\text{NO}_x\text{-N}$ mass budgets were determined (Venkatram et al., 1990). For all of the United States and Canada combined, 39% of anthropogenic $\text{SO}_x\text{-S}$ emissions were accounted for by wet deposition, 23% by dry deposition, and 4% by droplet deposition, and 34% of the emissions were exported from North America. For $\text{NO}_x\text{-N}$, 40% of anthropogenic emissions were accounted for by wet deposition, 26% by dry deposition, and 3% by droplet deposition, and 34% of the emissions were exported from North America. The urban perturbation accounts for 15% of the wet plus dry deposition for the United States and Canada combined.

It is interesting to note that both sulfur and nitrogen species in precipitation in Canada in this study exceed Canadian emissions, probably due to the overall net transport of emissions from the United States into Canada.

REFERENCES

- Sisterson, D.L., V.C. Bowersox, A.R. Olsen, T.P. Meyers, and R.J. Vong. 1990. Deposition Monitoring: Methods and Results. SOS/T Report 6, National Acid Precipitation Assessment Program, Washington, D.C.
- Venkatram, A., D. McNaughton, and P.K. Karamchandani. 1990. Relationships between Atmospheric Emissions, Acidic Deposition, and Air Concentrations. SOS/T Report 8, National Acid Precipitation Assessment Program, Washington, D.C.

ABSTRACT

Leach, J.H., Ontario Ministry of Natural Resources, Lake Erie Fisheries Station, R. R. #2, Wheatley, Ontario, N0P 2P0. Influence of the zebra mussel, Dreissena polymorpha on water quality of Lake Erie.

The European zebra mussel, Dreissena polymorpha (Pallas), is now well established in the Great Lakes system. Initial colonization may have occurred in 1986, likely from larvae discharged in ballast water, but mussels were not observed in Lake St. Clair and Lake Erie until June 1988. Large populations of the mussel are now established in these lakes. It has spread to all of the Great Lakes and is found from Cornwall, Ontario, in the east to Duluth, Minnesota, in the west. Dispersion has been aided by a motile larval stage and the ability of adults to attach to boat hulls with byssus threads.

The zebra mussel is a serious biofouling pest in Europe and is rapidly becoming one in North America. One of its most harmful impacts is the colonization of intake cribs and pipes serving water treatment plants, power generating stations and industries. Costs associated with prevention of infestations and removal of encrustations are projected at many millions of dollars.

Ecological impacts are also possible but are more difficult to predict and quantify. There is concern that some species of native mussels, and in particular the large unionids, may be in jeopardy because their shells are being colonized to the point where the mussels can no longer function normally. Although impacts on fisheries have not yet been measured, managers are concerned that the invader could affect fish production in two ways. The fouling of spawning reefs could affect reproduction of shoal spawners if the habitat is altered sufficiently to reduce egg deposition and survival. Preliminary results from observations on walleye in the western basin of Lake Erie indicated that reproduction and survival in 1990 were satisfactory. Secondly, the shifting of organic matter from pelagic to benthic areas through filtering by zebra mussels could disrupt the food web that links primary production to larval fish. Research to quantify this process and to determine its impact on the food web is currently underway in Lake Erie.

The zebra mussel has already affected water quality in Lake Erie and Lake St. Clair. The most visual impact is an increase in water clarity. Between 1988 and 1989 (May to November), mean Secchi disc transparencies increased 85 percent and 52 percent in the western and central basins of Lake Erie respectively. Preliminary data to September 1990 indicate that mean transparencies in 1990 were still greater than those in 1988 but less than those recorded in 1989. Resuspension of bottom sediments due to above normal winds during spring and early summer of 1990 probably masked the effects of the zebra mussels on water clarity. For example, transparencies in the western basin in August and September, 1990, were above those measured in the same period in 1989. Turbidity in Rondeau Bay has declined to the point where water clarity is probably sufficient to permit rooted aquatic plants to reestablish.

Mean concentrations of chlorophyll a declined 43 percent and 27 percent in the western and central basins of Lake Erie respectively between 1988 and 1989 (May to November periods). Preliminary results indicate a further decline in 1990, especially in the western basin. Dreissena is obviously competing successfully with filter feeders for phytoplankton. The production of faeces and pseudofaeces by Dreissena should favour other benthic organisms and early observations indicate an increase in gammarids in western basin reef areas. There is concern that a build-up of organic matter in the interstitial areas around the mussels could reduce dissolved oxygen concentrations through decomposition to the point where survival of fish eggs was adversely affected. However, a joint study with the Department of Fisheries and Oceans in April, 1990, indicated that dissolved oxygen was at or near saturation levels on walleye spawning reefs in the western basin of Lake Erie. Further studies are required to determine what happens to oxygen concentrations as organic matter and layers of mussels accumulate.

There are early indications that water taste and odour may be affected at water treatment plants (WTP) by Dreissena. Taste and odour problems occurred at the Windsor WTP in the summer of 1990 and were attributed to Dreissena either directly from the bodies of veligers and adults or indirectly from increased populations of aquatic plants because of improved water clarity. Additional research is required to delineate causes of taste and odour problems and also to determine to what extent Dreissena is improving water quality by concentrating contaminants.

CROSS-DISCIPLINARY ANALYSES OF ENVIRONMENTAL HEALTH STUDIES
SUGGEST THE NEED FOR NEW APPROACHES TO RISK ASSESSMENT

by

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A comprehensive examination of the literature on wildlife and human health in the Great Lakes basin provides incentive for new approaches to assess hazard from exposure to bioaccumulative, toxic substances. A review of the mechanistic actions of the contaminants commonly found in wildlife and human tissue further supports the need for change. Current public health strategies to measure population effects are too blunt to detect the subtle health decrements that may occur as a result of exposure to these chemicals. Breakthroughs in understanding the effects of a number of these persistent, pervasive organic chemicals are being made in the Great Lakes region by integrating research in wildlife, human, veterinary, and animal toxicology, ecology, epidemiology, and cellular and tissue biology. Following years of monitoring contaminants in the ecosystem, researchers in these disciplines are beginning to interpret what the concentrations mean in terms of wildlife health effects. This information provides new tools for public health authorities to assess the status of human health.

Sixteen top predator species in the Great Lakes basin have experienced severe reproductive problems accompanied by population declines since the 1950s. The health of many bird species showed marked improvements in the 1970s as the result of reductions in DDT and its metabolites producing thicker egg shells and improved reproductivity. Today, health problems that are just as serious but far more subtle than eggshell thinning are still reported in top predator species. Few overt symptoms are reported in adult animals -- instead, they are observed in offspring of exposed animals.

Health problems observed in wildlife offspring have been associated with elevated exposure to a number of contaminants. Researchers infer this exposure is the result of parental transfer through the egg, placenta, breast milk, and/or feeding of contaminated prey to offspring. Anomalies reported in wildlife offspring include: metabolic problems that cause low birth weight, loss of weight gain, and in some instances death from wasting; edema; birth defects; embryo, chick, fetus, neonate, and young adult mortality; behavioral changes; target organ damage; immune suppression; and abnormal sexual development.

An examination of the literature on the chemicals most often found in both Great Lakes wildlife and human tissues was undertaken. With one exception, (benzo a pyrene) these contaminants are not acute toxicants and genotoxicants, nor have they been determined unequivocally to be human carcinogens. They are developmental toxicants. Research at the cellular and tissue level shows that the mechanisms of action of the critical Great Lakes pollutants are often similar and general in nature. Most of the critical chemicals found in elevated concentrations in Great Lakes biota are capable of affecting normal metabolism and development in at least one or all of the following ways. First, they block cell to cell communication. Second, they induce enzymes in a number of tissues that enhance the excretion of hormones naturally produced by the endocrine system. And third, because of their chemical structure they have an estrogenic influence as well. All three mechanisms under proper timing and dose can lead to abnormal development. The cumulative effect of mixtures of these chemicals at the cell, tissue, and organ level is just beginning to be understood.

It is important to note that in laboratory animals a number of developmental health decrements have been associated with specific PCB, dioxin, and furan congeners and a number of pesticides including DDT and its metabolites, dieldrin, lindane, hexachlorobenzene, and others. These adverse health effects include wasting, edema, birth defects, immune suppression, target organ damage, effeminization of male animals, behavioral changes, and premature death, all in a dose-related manner; the same health decrements reported in Great Lakes wildlife.

Most importantly, except for a few fish species and the Beluga whale, cancer has not been reported in Great Lakes animals. Unfortunately, most risk assessments are based on cancer, not developmental effects, with the exception of mercury and lead.

A global search of the literature on residues of these contaminants in human tissues reveals they are found in all reproductive tissue, including breast milk. As a result, exposure during the embryo, fetal, and perinatal periods can be elevated on a weight to weight basis, coinciding with a period of rapid development that sets the course of development through maturity. Recent laboratory studies using a number of these chemicals revealed that obvious health effects may not be fully manifested until adulthood in exposed animals. Using wildlife and animal studies as models to assess human health, new technologies are needed to measure human exposure as well as new approaches to measure the possible cognitive, behavioral, and social effects of developmental toxicants.

ENVIRONMENTAL CONCERNS - KEEPING OUR PERSPECTIVE

John P. Nunan, P.Eng., President
Trow, Dames & Moore

INTRODUCTION

This talk is intentionally provocative. The purpose of the presentation is to put before you a number of current, relatively high-profile, environmental concerns, and to discuss these in brief so as to stimulate thinking as to the type of research that might be undertaken to enhance knowledge of these issues, and putting them in truer perspective as they may affect public health and safety, and the quality of our physical environment.

Four concerns (issues) have been selected for discussion, not necessarily because of their importance, but rather due to the fact that these issues have been around for some time with little growth in our understanding of their true significance and seriousness. They are also issues that are causing much concern to various segments of the community and expenditures of large amounts of money to mitigate, possibly with less than adequate understanding as to why or if such mitigation is effective, or really required.

As Professor P.H. Jones has said, "society is engulfed in fear". This fear is not based on scientific findings, which have demonstrated that harm can result. It is based more on our ability to detect certain substances in our environment which we have discovered can adversely affect humans if ingested in large quantities. It is wrong to equate, in the minds of the public, the mere detection of a substance with ghastly public health threats. Such concerns have tremendously complicated life and in several instances have brought some forms of desirable development to a grinding halt. Some specific issues causing these concerns will now be discussed.

1) Methane Gas

Methane is a naturally occurring light hydro-carbon gas that results from the biodegradation of carbonatious material in the absence of oxygen. Methane is very widespread in nature and comprises approximately 95 percent of natural gas. Methane is produced in significant quantities during anaerobic decomposition of solid wastes in garbage dumps. It is also produced in earth fills where relatively small quantities of biodegradable material such as grass, brush and swamp debris has been incorporated in the fill. Methane can migrate from its location of generation to accumulate in buildings and other works where ignition of the gas has resulted in destruction of buildings and loss of life.

Today, the measure of a methane hazard or risk is usually determined by the insitu concentration of the gas. Is this appropriate? Is there a better way to evaluate the hazard? Is it really necessary to restrict development as much as we now do because of the presence of high insitu concentrations of methane? Are there, or can there be developed reliable methods of measuring methane flux directly, which, when compared to conservative estimates of building ventilation, will show when a buildup

of methane is so improbable that development of a particular site should not be constrained?

The issue of methane recovery from large, or even small garbage dumps, seems to offer a potentially attractive opportunity for energy recovery. This is already being achieved at some very large landfills, where the cost of energy is high and a suitable market for that energy is available. Some of the questions that need to be answered through research include: What are the conditions that enhance the rate of methane production? Is it better to keep landfill dry so as to restrict the rate of methane production, which also delays stabilization of the landfill, or is it preferable to develop sanitary landfills so as to enhance methane production? How would the recovery and use of methane from a landfill, where methane production was intentionally enhanced, compare economically with other forms of waste recycling for energy, conservation and recovery, such as the burning of refuse-derived fuel from waste? What do we know about the character of the solid waste that goes into our Canadian landfills? Are we perhaps missing opportunities or even aggravating conditions by some current practices such as removal of materials from waste streams that would produce methane, when the cost of reusing these materials in other ways is less attractive?

2) Nitrates In Groundwater

Nitrate which is an essential compound for plant growth and which is naturally produced in the environment by bacterial activity and to a much smaller degree, by electrical storms in the atmosphere, has become a major concern relative to the potable use of groundwater. The use of nitrate in fertilizers to increase food crop yields in rural areas and the heavy use of nitrogen fertilizers to grow green lawns in urban areas is increasingly suspected as being the cause of nitrate buildup in groundwater, which in many areas has risen to fifty percent, or more, of the accepted 10 ppm for drinking water. This change has caused concern that the trend will continue, which in turn has resulted in rejection of some well supplies intended for municipal use, even though all other quality and quantity factors are favourable. The limit of 10 ppm has been conservatively accepted as a safe limit for consumption by infants who are more susceptible to nitrates than are older children and adults. A question we should perhaps ask is: should these sources of water supply be rejected because of an increasing nitrate trend, when the content is still well below the accepted health standard? Does the trend mean that the nitrates will in fact rise above the limit? It can be shown that the use of fertilizer for cash crops will theoretically increase nitrates in groundwater over broad areas of intensively cultivated land by as much as five parts per million, but that level should not rise much higher under prevailing climatic conditions. The level of nitrate in water at a specific sampling point may not establish the content in the water from a heavily pumped well that draws water from a broad area of one or two square miles. Do we really know at what level nitrates significantly affect the health of humans? Can we demonstrate by research how significantly agricultural fertilizer affects groundwater quality? Are we rejecting plentiful supplies of water because of concerns over nitrate buildup and trace amounts of other agricultural chemicals where detailed study may show that this is unnecessary?

3) Landfill Leachate

Leachate is produced in landfills when precipitation percolates through buried solid waste, when waste is deposited below the water table, or when the water table rises into waste because a thick pile of slowly permeable waste alters the local hydrologic regime. Dissolved in landfill leachate are constituents of virtually everything that is in the waste itself and indeed some compounds that are produced by the mixing and interaction of solutes from waste. Leachate is for the most part, produced under anaerobic conditions and has a putrid odour. Because leachate contains many known, and suspected but unknown, water pollutants, great emphasis has been placed recently on the containment of landfill leachate by lining garbage dumps, and attempting with no proven success to cover them so as to restrict infiltration of precipitation. Recognizing that leachate accumulates, it is drawn off and disposed of in waste water treatment plants. Unfortunately, very little hard data exist on how effectively leachate is renovated by conventional secondary waste water practices. We know that BOD is reduced. We know that VOCs are removed; but to where, to the atmosphere? What is the fate of soluble inorganics? They are undoubtedly diluted before release to surface streams, but do they still persist to impact surface water?

Is secondary waste water treatment really superior to the attenuation treatment and dilution that takes place naturally in the soil beneath and around landfills as the leachate is carried slowly by groundwater? We know from experience that leachate contaminated groundwater beneath some very large landfills is renovated by natural processes within a few hundred metres of the landfill. Is this a legitimate use of a small segment of the natural environment? We know the effect will not be permanent. Have we made any quantitative studies to compare the effectiveness of natural subsurface treatment with conventional waste water treatment practices? What are the cost implications? Are we creating problems by making our waste dumps too large? Do we in fact know how seriously leachate affects health? Are there any authentically documented cases to show that waste residues in groundwater affected by landfills have actually made people sick? What evidence have we that artificial containment systems actually stop leachate escape permanently?

In summary, are garbage dumps the alleged monstrous insult to the environment they are thought by many to be, or do they indeed represent a legitimate, temporary use of very small segments of the physical environment? The actual land area used for sanitary landfill is relatively small in spite of the popular contention that we are burying ourselves in our own waste. Have you ever, on a clear day flying for one hour between Montreal and Toronto tried to locate the sanitary landfills? It is difficult, because they are on that scale very small and far between. If we attempted to prove that landfills are a legitimate land use rather than to look microscopically at their adverse effects, might we discover something useful?

4) Soil Classification Criteria For Landfills

In Ontario, disposal criteria have been developed which are designed to control the chemical quality of contaminated soil that, under Ontario Regulation 309 and the Decommissioning Guidelines, must be removed from decommissioned sites. Unfortunately, these rigorous criteria have caused a lot of inert material to be diverted to expensive and already

severely burdened sanitary landfills, when much of the material would be perfectly safe if left where it was, or used to "make ground" for useful development. If the soils are classified as registerable waste or subject waste, the transportation and disposal cost in the Toronto region may range from \$80.00 to \$250.00 per tonne, depending upon the haul distance and character of the material.

The definition of inert fill is so broad that what constitutes inert is often a matter of opinion. Operators of "clean fill" sites are frequently unwilling to accept material if there is doubt as to its origin or chemical content. As a result, sites for disposal of marginally contaminated soil are very scarce.

Prior to acceptance by a municipal landfill, chemically contaminated soil of the type described above must be classified according to Ontario Regulation 309. The Regulation 309 classification procedure involves an acid leach test and comparison with criteria set out in Schedule 4 of the Regulation. Soils that leach less than 100 times (X) the Schedule 4 criteria are acceptable at a municipal landfill subject to further classification as to whether the soil is non-registerable (<10X the criteria), registerable (10 to 100X the criteria) or inflammable.

In my opinion, key questions that need to be addressed; particularly, for soils that are classified as non-registerable are: Is disposal of such soils at a municipal landfill responsible management of scarce landfill capacity? Certainly, in the Toronto area this is a valid question; particularly, when such soil has not generally been utilized for daily cover but rather incorporated into the waste cells? A possible answer may be that in the short term, revenue from receipt of materials classified as waste is considerably higher than materials received for top cover.

Is the current Regulation 309 leachate extraction procedure a proper method of evaluating disposal options for marginally contaminated soils in southern Ontario where conditions are naturally alkaline and where mono disposal of such soils would seem to be the preferred and most cost effective disposal option?

ION MOBILITY SPECTROMETRY IN ATMOSPHERIC ENVIRONMENTAL MONITORING
IN THE US SPACE PROGRAM, G.A. Eiceman, Department of Chemistry,
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ABSTRACT

The utilization of chemical instrumentation, originating with military establishments, for monitoring atmospheric environmental quality in domestic and space applications represent a little known and potentially rewarding example of technology transfer. Human exposure to hazardous airborne organic vapors at trace levels presents challenges in areas of risk assessment, toxicology, and technology of chemical sensing. Since ca. 1965, improvements in laboratory tools for measuring contamination have kindled interest in health effects from exposures that previously were disregarded. Still, refinements in toxicology, risk assessment, and human protection in those instances were dangers are certain have been hindered by limitations in chemical analysis of environmental and biological samples. While extraordinarily advanced tools for chemical characterization of samples are available, the expense and associated mechanical or electrical requirements of such instruments preclude uses in routine or continuous manner. As a result, the philosophy of environmental analysis has remained stagnant for the last two decades in spite of impressive sophistication of chemical instrumentation. A shift toward continuous monitoring or at least small portable chemical instrumentation is necessary and has been hindered only by the inherent properties and behavior of available technologies for chemical sensing.

Ion mobility spectrometry (IMS) is a derivative technology of a family of ionization detector based upon the conversion of hazardous vapors to ions in air at atmospheric pressure. In IMS, the ions are largely intact, though ionized, molecular species that can be analyzed for speed of movement in a weak electric field. This speed or ion mobility provides a measure of individual chemical constituents through the relationship of size-to-charge rather than mass-to-charge used throughout mass spectrometry. Thus, IMS can be viewed as an advanced smoke alarm where the ionization of atmospheric contaminants is followed by a rapid determination of the physical or chemical characteristics of the same ions. Advantages to IMS, in principal, include small size, low power, and trace detection limits but these were not realized until 1985.

Early developments of modern IMS can be dated to ca. 1965 when a military contract resulted in prototype hardware designs. Commercial versions were publicized in 1970 and several research groups, each with a particular developmental or investigative emphasis. Despite the demonstrated favorable response of IMS toward an impressive range of chemical classes, IMS was regarded widely as potentially significant but with serious limitations in selectivity and reliability. Studies during the last decade have shown these reservations to be rooted in the particulars of mechanisms of ion formation at atmospheric pressure rather than in ion mobility measurements.

Extensive in the consideration of IMS for environmental monitoring was the decision by the US and UK defense establishments to refine IMS for chemical warfare agent detection on battlefields. Ramifications in the use of instrumentation, formerly considered delicate and cumbersome, in such a hostile environment included rugged, simple, and hand-held designs with refined ionization chemistry for integrity of response. In short, IMS was converted from a laboratory tool to a field monitor in a manner unlike any previous chemical analyzer. Present estimates of military distribution suggest an expansive role for IMS in armies of most western governments.

Instrumentation worthy of combat environments provided an impetus to explore civilian applications and in two instances found niches in the US space program. These two applications that are currently in testing or developmental stages include screening for vapors of hydrazines in the shuttle air lock and the use of portable gas chromatography/ion mobility spectrometry (GC/IMS) as a total hydrocarbon monitor for ambient air. In each instance, a fundamental obstacle to the utilization of IMS as envisioned and the primary emphasis of our research program has been the description and refinement of the chemistry of ionization. These will be discussed as used for the effective transfer of military IMS to environmental monitoring.

E1 Fostering Technological Transfer: Enabling Conditions
in the Firm and in the Market; B. Hull, The Conference
Board of Canada, Ottawa, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

UTILIZATION OF ENVIRONMENTAL RESEARCH TO CONTROL LEAD CONTAMINATION

by

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ABSTRACT

Due to the lack of well founded guidelines in the United States and other countries for lead contamination in soil, a special Society for Environmental Geochemistry and Health (SEGH) task force was formed to utilize research data and actual case studies to develop a report on recommended guidelines for Lead in Soil. An action oriented plan on how to systematically evaluate lead contamination for the protection of public health or determine lead levels to be used for remedial actions will be presented with examples of how to determine action levels for control or remedial measures associated with lead contamination problems.

INTRODUCTION

Technology transfer is a scientific terminology that implies many different interpretations dependent upon how it is used. In the United States, the Federal Technology Transfer Act (FTTA) of 1986 was passed to help remove perceived barriers for collaboration and utilization of research between the public-private sector. The preamble to the FTFA bill also noted that "many new discoveries in science occur at universities and federal laboratories while the application of this knowledge depends upon industry." (Nichols, 1990). However, technology transfer is often easier to propose than to implement due to the following constraints:

1. Cultural resistance encountered within countries and specific locations.
2. Time requirements before profit payback.
3. Necessity to also transfer appropriate training to carry out new technology.
4. Uncertainties of legal or regulatory requirements.

Our present time of environmental awareness has received further intensification by current environmental crises (such as the Alaskan oil spill, etc.), so that the public demands a more rapid transition of environmental research methodologies into practical applications. One major difficulty is how to evaluate research and transfer selected laboratory or field methodologies as rapidly as possible into a new or improved technology. For

example, in Canada, the proposed process of converting sewage sludge into fuel, has the potential of replacing over 700,000 barrels of oil at a possible savings of over \$28 Million at present oil prices which may continue to increase in the present unstable geopolitical mid-east crisis (Nichols, 1990). While this may serve as a good model to illustrate technology transfer, industry is often reluctant to invest in many processes because of the difficulty in receiving government approval for the technology proposed. Environmental research may also be utilized for the development of guidelines such as the control of lead contamination and allow for the use of appropriate technology, including remedial actions, to be approved by public health officials and regulatory agencies for use by concerned industries.

USE OF ENVIRONMENTAL RESEARCH

The absence of scientifically recognized guidelines in the United States, as well as other countries, concerning the acceptable concentration of lead in soil (Davies and Wixson, 1987) has contributed to confusion by regulatory agencies, industries, public health officials, the medical community and concerned citizens (Lead in Soil, 1988). The questions most often asked focus on possible adverse health effects and risks from lead exposure or the recommended permissible soil lead concentration to be used for remedial action at contaminated or hazardous waste sites (Davies and Wixson, 1986).

Preventive measures or control technologies are usually not applied when there is an uncertainty of regulatory requirements. Therefore, environmental research data from around the world was utilized by a Society for Environmental Geochemistry and Health (SEGH) task force in developing a report on recommended guidelines for "Lead in Soil" (Wixson, 1988). This report illustrates how cooperative efforts between industries and regulatory officials may be applied to determine the risk of human exposure to lead (Davies and Wixson, 1989). The methodology used in this report also shows how environmental research can be applied to develop guidelines necessary for the application or control of remedial technologies.

The SEGH task force was formed in 1988 to address the problems, evaluate data and develop scientific recommendations concerning lead in soil. The risk assessment steps of: 1) hazard identification; 2) dose-response assessment; 3) exposure assessment; and 4) risk characterization were used to develop a "Phased Action Plan" (illustrated in Figure 1) which evaluates the relationship between blood lead levels and the levels of lead in soil as one possible source of exposure. The "Phased Action Plan" also required extensive review of research data and case studies for the development of a target soil lead/dust lead guideline model derived from the use of documented health criteria.

The factors associated with Lead and Health are concerned with the population groups at risk from the possible adverse health

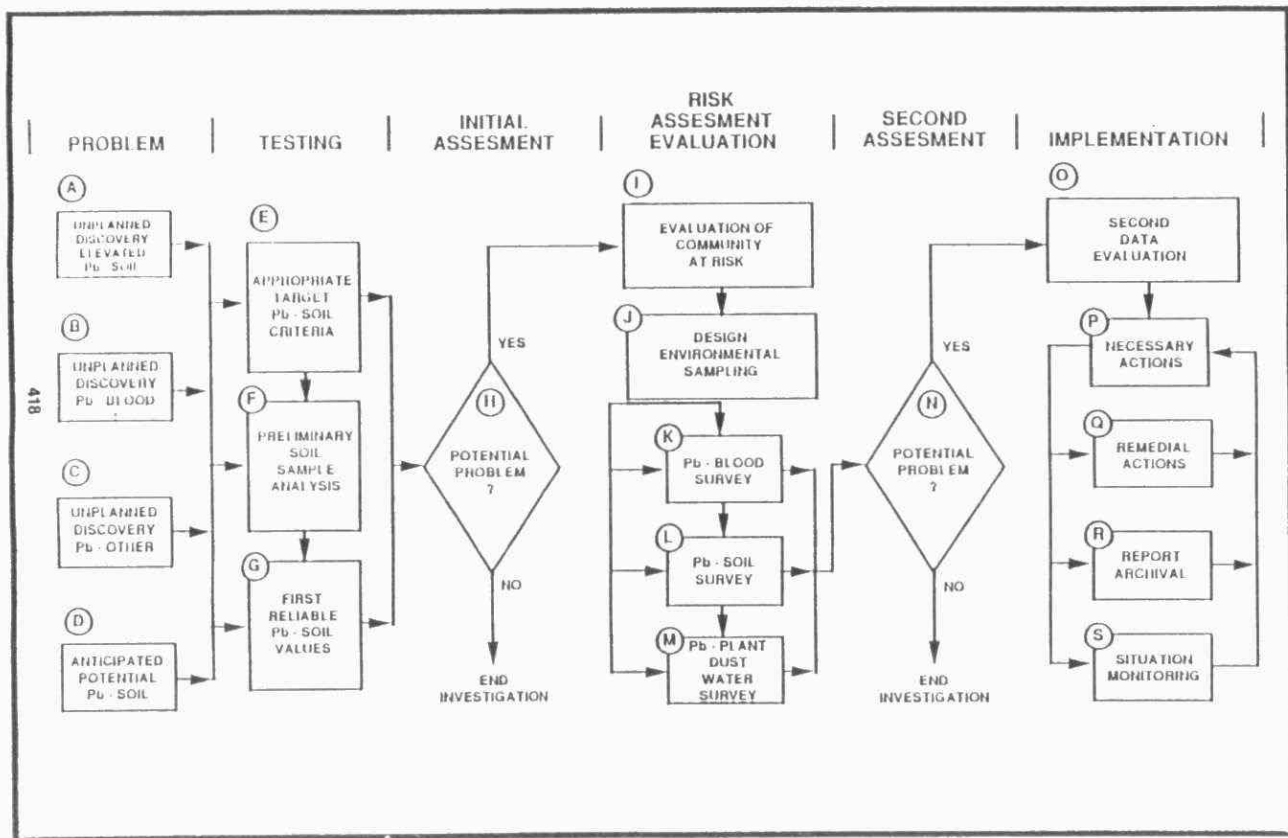


Figure 1. Phased action plan for lead in soil

effects of lead. Therefore, health criteria and research data were used in deriving a target soil/dust lead guideline concentration.

A single number for a lead in soil guideline for the protection of young children was considered unrealistic for a number of reasons. The population at risk can itself vary; therefore, the soil/dust guideline was established as a relationship or formula, in order to allow for a variety of environmental situations and regulatory criteria.

In the model developed, blood lead concentration was equated to a baseline level plus an increment resulting from exposure to soil or dust lead. The model also takes account of the chosen blood lead guideline or target concentration and the degree of protection required for the population. The slope of the blood lead-soil lead relationship is then used in calculating an increase in blood lead over a baseline value. Hence the soil guideline, can vary depending on a variety of factors, allowing this response to be adjusted for a given situation with the opportunity of being modified as more research data become available.

The derivation of the blood lead/soil lead model is illustrated in Figure 2.

The major uncertainty in the use of such a relationship is the value to use for δ , the response of blood lead to increasing soil or dust lead concentration. It therefore appears that a value in the range of 2-5 would be appropriate for most situations and that the major influence on a value for δ may in fact be child activity rather than any characteristics of dust or soil.

RISK MANAGEMENT

The risk management section of the SEGH report emphasizes the exposure assessment and development of a relationship between blood lead levels and the concentration of lead in soil to formulate suggested guidance for acceptable soil lead. Geographic and physical processes that affect soil lead accumulation are discussed along with social aspects of lead contamination and other risks.

Legal aspects and cleanup levels for lead are presented along with economic considerations of appropriate technology utilized for remedial actions.

SUMMARY

The lack of guidelines or regulations often contribute to difficulties in implementation of improved technology for the control of metal contamination. The use of environmental and human health research data coupled with case studies of lead contamination have been used by a SEGH task force to develop a

TARGET SOIL/DUST LEAD GUIDELINE MODEL
DERIVED FROM USE OF HEALTH CRITERIA

$$S = \frac{\left| \frac{T - B}{G^n} \right|}{\delta} \cdot 1000$$

where:

S is the soil or dust guideline, a geometric mean concentration in μg Pb per gram of dust (ppm)

T is the blood lead guideline or target concentration, in μg Pb/dl whole blood

G is the geometric standard deviation of the blood lead distribution, typically in the range of 1.3 to 1.5

B is the background or baseline blood lead concentration in the population from sources other than soil and dust

n is the number of standard deviations corresponding to the degree of protection required for the population at risk, and would normally follow from the way in which the blood lead guideline T was defined

δ is the slope or response of the blood lead - soil(dust) lead relationship and has the units of μg Pb/dl blood increase per 1000 ppm increment of soil or dust lead

Figure 2.

Derivation of the blood lead/soil lead model

report on recommended guidelines for lead in soil. These guidelines are necessary to control of lead contamination by recommending action levels to protect public health. Recommended levels of lead contamination in soil also may be used to determine how clean is clean? when remedial action is necessary.

ACKNOWLEDGEMENTS

The support of the Society for Environmental Geochemistry and Health, the International Lead Zinc Research Organization, Inc., the Lead Industries Association and the US Environmental Protection Agency is acknowledged. Special thanks also to the members of the Lead in Soil task force for their time and effort on this important project.

LITERATURE CITED

Davies, B.E. and Wixson, B.G. 1986. Lead in soil: how clean is clean? In: Trace Substances in Environmental Health-XX, Hemphill, D.D., Ed., University of Missouri-Columbia, 233-241.

Lead in Soil: Issues and Guidelines. 1988. Davies, B.E. and Wixson, B.G., Editors. Science and Technology Letters, Surrey, England.

Nichols, A.B., 1990. Moving research from the lab into the field. In: Water, Environment and Technology. Water Pollution Control Federation, Alexandria, Va., U.S.A. Vol. 2, No. 10, 48-55.

Wixson, B.G. 1987. Lead in soil: issues and guidelines conference. In: Trace Substances in Environmental Health, XXII, Hemphill, D.D., Ed., University of Missouri-Columbia, 349-356.

VOLUME II
PANEL PRESENTATIONS

"GLOBAL WARMING: WHAT IS AT STAKE?" - Panel Discussion

THE INTERNATIONAL SCENE: J. P. Bruce

With the first assessment report of the Intergovernmental Panel on Climate Change (IPCC), and the Second World Climate Conference (SWCC) completed, discussion of greenhouse gases and climate change are now moving to a more formal stage of international negotiation of a Convention on Climate Change. The positions taken by various countries at the IPCC meetings and the debates at the SWCC give clear indications of some of the major issues that will have to be addressed in negotiation of a global Convention. These issues will be identified and some possible means will be suggested of addressing the diverse concerns.

Major changes in both environmental and economic policies, especially in the energy sector, will be needed in most countries if an effective international agreement is to be reached.

GLOBAL WARMING: A CANADIAN PERSPECTIVE AND ACTION STRATEGY

Dr. D. Kirk Dawson
Director General
Canadian Climate Centre

Climate Change is perhaps one of the best examples of global interdependence of countries. An effective response will require a global effort which is likely to have considerable impact on human kind. A major dilemma, however, is that actions may be required well before many of the specific issues can be analyzed more thoroughly by further research.

Some of the more stringent actions that may be required, particularly those which serve to limit emissions of greenhouse gases, will have a profound effect on national policies in all areas. The manner in which nations address this issue will have major implications for trade and economic balance, between industrialized and developing countries, between industrialized nations themselves and within the different regions of individual countries.

Canada has played a significant role in seeking international solutions. We have been an active participant on the Intergovernmental Panel on Climate Change (IPCC) and are strong proponents of the negotiation of a comprehensive global convention on climate change.

At home, Canada supports a world-class climate research and impacts program and is now working with the provinces to conclude a National Action Strategy on climate change. The strategy will be:

- Comprehensive. It will deal with all of the major sources of greenhouse gases and the sinks of those gases;
- National in Scope. It will contain strategies appropriate for all levels of government, as well as industry and individuals, while recognizing that climate change is a global problem requiring international cooperation; and
- Action-oriented. It will be a cost effective and flexible action program that is based so that it can respond to new understanding and developments in the future.

Global Warming: What Is At Stake? Socio-economics

Erik Haites

In relation to global warming, socio-economics could cover many issues. To meet my time constraints, I must limit the scope of my presentation.

I will not discuss the socio-economic consequences of global warming, nor the socio-economic implications of adaptation to climate change. For Ontario, these were reviewed at a workshop organized by the A.E.S. in November 1985. A summary of that workshop is available in the Climate Change Digest (CCD 88-08) "CO₂ Induced Climate Change in Ontario: Interdependencies and Resource Strategies."

Today, I will focus on two socio-economic aspects of global warming that are the subject of more current research. They are:

- the costs of achieving reductions in emissions of greenhouse gases, and
- the potential application of economic instruments to reduce greenhouse gas emissions.

Following the Toronto Climate Conference in June 1988, analysts started to examine how the proposed interim target of a 20% reduction in 1988 emissions of CO₂ by 2005 could be achieved. I reported on such an analysis for Canada at this conference last year. During 1989 and early 1990, studies were completed for a number of countries. The universal conclusion is that the Toronto Conference target is a tough one. Virtually, all currently available CO₂ emissions abatement measures will need to be implemented to their full technical potential to reach that goal.

Once the measures needed to achieve the target are known, people want to know the cost of implementing those measures. Although some preliminary answers are available, this is a matter that is currently under intense study.

The preliminary cost estimates range from about -0.3 to +0.5 percent of GNP annually to 2005. Some studies show net savings, as a result of lower energy consumption, from measures to reduce emissions of CO₂. Other studies show a net cost for these measures. The results tend to vary systematically with the methodology used.

Typically, energy efficiency measures account for the bulk of the CO₂ emissions reductions to 2005. Studies that analyse the economics of individual energy efficiency measures, find most of these measures to be attractive from a societal perspective. They assume that the measures are implemented as part of the normal replacement cycle. This yields an overall saving as a result of implementing the CO₂ emissions reduction measures. Studies for Canada and Australia are good examples of this approach.

The other approach to estimating the cost of CO₂ emissions abatement is to use a macro-economic model. A carbon tax is used to achieve the target reduction in emissions. The tax revenues are recycled so that there is no net loss to the economy. Studies of this sort for the U.S., Japan, and other countries, all yield positive costs for CO₂ emissions reduction.

The carbon tax approach causes all energy users to adjust their energy consumption and equipment at the same time, reflecting the introduction of the tax. Adjustments do not reflect the replacement cycle for energy using equipment, thus raising the adjustment costs. On the other hand, assuming that all adjustments occur as part of the normal replacement cycle and that the adjustment costs of the equipment producing industries are reflected in the

equipment prices, undoubtedly understates the adjustments. There are probably other reasons as well for the differences in the cost estimates produced by the two methodologies.

In any event, the first order estimates of the cost are between -0.3 and +0.5 percent of GNP. Research currently underway will refine these estimates and provide a better understanding of the nature and magnitude of the costs.

Economists believe that policies, such as emissions charges or tradeable emissions permits, can achieve a specified environmental target at lower overall cost than emissions regulations. Given the scale of the emissions reductions proposed by the Toronto Conference target, cost-effective policies are doubly important. I stressed the need for such policies in last year's session.

Tom Tietenberg and I have outlined a linked system of emissions permits and emissions taxes for carbon dioxide and other greenhouse gases. Briefly, the system is as follows. Each country is assigned emissions targets by international agreement; developing countries would probably have targets greater than current emissions and developed countries might have targets 25 percent below current emissions.

Within a country, such as Canada, large sources could earn permits for reductions beyond their target. Other large sources, such as industries, electric utilities, and large commercial and institutional facilities, could purchase permits in order to reach their target reduction. The fuels used by smaller sources, residences, vehicles, and small commercial facilities, would include an emissions tax equal to the market price of the permits. Thus, all sources have the same target reduction and the same cost per unit of CO₂ reduced.

International trade in permits would be allowed. However, each country could establish import and export restrictions. Developing countries could

restrict trades between subsidiaries and parent companies if they chose. A country could restrict imports from countries whose permits it judged to be of dubious value. These arrangements provide economic incentives to participate in the international agreements for control of greenhouse gases. And, they provide enforcement mechanisms without requiring an international inspectorate.

The system, we believe, could be extended to CFCs, many sources of methane emissions and afforestation, but not to nitrous oxide, ozone, or ground level ozone precursors.

In conclusion, policy analysis of global warming is proceeding at a very rapid pace. Last year, the potential abatement measures and the scale of the response required were just being determined. They are now fairly well known and preliminary estimates of the associated costs are available. These cost estimates are being refined and appropriate policies are being formulated. Next year, I hope that we will know what policies are to be implemented in Ontario, in Canada, and internationally.

WARMING TO A CRISIS:
THE MEDIA AND CLIMATE CHANGE

Abstract for a speech

By Michael Keating
Environment Writer and Consultant

to

The Technology Transfer Conference of Environment Ontario
Royal York Hotel
November 20, 1990

Global warming hit the front pages in Canada in October, 1983. This came immediately after the New York Times broke the story of the EPA report by John Hoffman, saying the greenhouse effect would begin in the 1990s.

This led to a small flurry of stories, which grew slowly but steadily into a trickle, and, over the last few years, into a flood.

The pace of coverage picked up in the mid-1980s as more of the big media, such as Time Magazine and the TV networks, caught on to climate change as a mega-story. There was talk of a threat to human life.

It was and is a great story for graphic images. Belching smokestacks and burning forests. Kentucky winters in Toronto. Glaciers crashing into the sea as the ice caps melt. Waves lapping at the doors of Wall Street. Two, three or four Prince Edward Islands. Florida going back the the alligators. Hurricanes with 40 to 50 per cent more punch than now.

People even coined the term "heat beat" for reporting on climate change.

The story got a real boost in 1988 when reporters had both the devastating heat waves in central North America and the Toronto conference on the changing atmosphere. And that was when James Hansen of NASA told the U.S. Congress that he was 99 per cent sure that climate change had begun.

The seriousness of the issue was reinforced by the record drop in the Mississippi River and ensuing calls from some U.S. politicians for water diversions from the Great Lakes.

So, how have the media covered the science of global warming?

Since the early 1980s, reporters have generally accepted that climate change is a real and poses a serious threat. They have given relatively little coverage to scientists, or politicians, who say this is just a theory.

I think reporters feel global warming is a fairly easy concept to grasp. Humans put billions of tonnes of gases into the atmosphere. Billions is a big number, so it must have an impact.

Reporters have generally treated climate change as a "bad thing" but that has not been universal. There are still some stories about the benefits of warmer winters and less snow.

How responsible have the news media been in reporting on global warming? By and large the reporting that I have seen has been fairly accurate. It has been much better than coverage of some issue such as PCBs.

But whether or not you like the coverage so far depends a lot on what hat you are wearing.

If you are a scientist who believes that global warming is a problem, then you are probably happy with the fact the media have made the greenhouse effect as common a phrase as acid rain. I think the environment movement feels the same way.

If you are a scientist who believes it is just a theory, then you probably feel the media have not been critical enough of the other scientific camp.

If you a minister of environment and have been in the portfolio long enough to understand the issues, then you probably like the coverage. You will hope that the media put more pressure on the premier or prime minister and the minister of energy to come up with greenhouse gas strategies.

If you are the minister of energy you probably wish the media would stick to covering the deficit or the ups and downs of the stock market.

If you work for the oil and coal industry you probably don't want to open your paper in the morning.

Where will news coverage go in the future?

The media are on to the fact that, per capita, Canadians are the world's greatest energy users and one of the world's greatest producers of greenhouse gases.

Where will the mud from this kind of coverage stick?

That's very hard to predict. A lot depends on the critics and on scientific research that is released to the public.

We have already seen considerable criticism of the coal-burning power plant at Point Aconi, Cape Breton, and some criticism of Hibernia in the east, and heavy oil projects in the north, because of they will all add CO₂ to the atmosphere.

There is an increasing number of stories about CO₂ from automobiles but the media have an ambivalent role in this one, since most reporters drive cars, and the media get a lot of revenue from auto ads.

The media face at least two difficult tasks ahead.

One will be in deciding when to report that global warming has started. The second will be in focussing on what to do about the problems.

Expert groups, including the Toronto atmosphere conference, suggested that the world should start switching to low or no carbon fuels such as hydro-electricity, wind, solar power, natural gas, biomass and possibly nuclear energy, if it can be made safe and if its use does not lead to more nuclear weapons.

We are also hearing calls from less developed nations for massive assistance to help them cut or avoid the emission of greenhouse gases while reducing poverty, hunger and disease.

These are complex stories, often without a clear set of targets to shoot at. Reporters are going to need lots of help from the scientists, policy makers, researchers, environment groups and others.

I remember quoting the Brundtland Report as saying we need lifestyles that are, "within the planet's ecological means." And I remember asking Maurice Strong if humans can make that kind of shift quickly enough. He said, "it is going to be a race between our sense of survival and our more indulgent drives."

What we need now is articulate spokespersons who will tell the public, through the media, how we are going to win that race.

* * *

1990 TECHNOLOGY TRANSFER CONFERENCENOVEMBER 20, 1990ABSTRACT OF J.D. McFARLAND'S REMARKS

The potential for global warming has become one of the most complex and hotly-debated issues in the energy/environment dialogue. Although there appears to be an emerging scientific consensus that an enhanced greenhouse effect is real, many uncertainties remain with regard to the magnitude, timing and regional effects. Canadians as yet do not fully understand the implications of this issue on public policy development nor the economic consequences of potential policy measures to address it. The energy industry is vitally concerned about promoting sound public policy in this area, and Imperial Oil has been active in providing a perspective on the issue in the context of domestic and international energy use. Imperial's initiatives to generate a broader understanding of the scientific and economic implications for Canada and Imperial are discussed.

J.D. McFarland/w1
October 5, 1990

Global Warming: What's Known and What's Not?

Bunli Yang

Global warming and what industrialized societies might do about it have become topics of intense debate. Apart from its importance as an environmental issue, and it is often regarded the most serious threat to the global environment, global warming has many uncertainties. That kind of uncertainty generates debate and may be a barrier to action.

It is straightforward to list what is known about global warming and climate change:

- there is a natural greenhouse effect in our atmosphere because of gases that trap heat;
- the natural greenhouse effect accounts for a warming of about 33 C.;
- the climate of an ice age differed from today's by a small change in average temperature, about 5 C.;
- in the past, average temperatures and concentrations of the greenhouse gases have been high together and low together;
- human activities have been increasing the concentrations of the greenhouse gases in the atmosphere;
- the impacts on climate of rapid changes in temperature will not be uniform;
- climate is inherently global, and international agreement on actions will be very difficult.

The list of unknowns is, of course, endless. They range from the physical science of clouds and oceans to the economics and the social impacts of climate change. Examples are the rise in sea level for any level of greenhouse gas concentrations, or the rate of temperature rise, or the amount of precipitation and soil dryness because of any warming, or the costs of prevention, or the costs of adaptation to climate change. The risks of climate change, though not known or even knowable, are widely regarded to be major.

While these unknowns may loom large, uncertainties about usual economic trends are even larger, but are not barriers to economic policies and actions.

For purposes of public policy, the relevant question is not "How much needs to be known with high certainty before taking action?" but "What should be done now, by whom, in the face of the risks?"

VOLUME II

SESSION C

LIQUID & SOLID WASTE RESEARCH

VERBAL PRESENTATIONS

MANUAL FOR ESTABLISHING VEGETATION
ON EROSION-PRONE LANDFILL SLOPES IN ONTARIO

N. DeFraeye and T.W. Hilditch,
Gartner Lee Limited, Markham, Ontario

I Introduction

The Ontario Ministry of the Environment (MOE) was concerned with the problem of erosion on landfill sites throughout the province. Up until 1986 the extent of the problem had not been documented in Ontario.

In 1987, a three year study was undertaken by Gartner Lee Limited (GLL), commissioned under the MOE, the goal of which was to develop a practical approach to remediate erosion on landfill sites via proper vegetation establishment and management.

The end products of this study were:

- a technical paper documenting the problem of landfill cover erosion in Ontario, complete with the results of test plot revegetation research across the Province; and
- a Provincial Landfill Revegetation Manual for landfill operators to provide guidelines on the establishment and management of vegetation on landfill covers for the prime objective of erosion management.

II Study Approach

Our activities during the study, concentrated on three components:

- an overview of erosion of landfill sites in Ontario;
- identification of the best revegetation techniques; and
- establishment of demonstration plots throughout Ontario.

To gain an overview of erosion on landfill sites in the Province, a questionnaire was developed to solicit information from individuals who have first-hand exposure to landfills occurring in a range of conditions. The questionnaire was distributed to the Abatement Officers at 22 District Offices of the MOE throughout the Province. As their responsibility includes the enforcement of proper landfill management, it was felt they could provide a current and objective view on landfill erosion throughout Ontario. Responses to the questionnaire provided an appraisal of landfill erosion on 52 landfills throughout the Province. This was screened down to 24 sites (4 in each of the 6 MOE Regions) for the collection of physical and biological field data.

Concurrently, literature from throughout North America was reviewed, in order to gain an understanding of the problems of landfill erosion in other jurisdictions. As well, techniques for site preparation, planting, and maintenance were evaluated.

Initial fieldwork included a visit to the twenty four sites which had been selected to represent the wide range of geographic and physical settings in which landfills have been located in Ontario. The selected sites included both operating and closed landfills. Of the 24 sites which were examined, all of the open sites and 83% of the closed sites suffered from erosion problems. Our literature review indicated that the problem is not limited to Ontario.

III The Problem

Not only does the widespread occurrence of landfill erosion in Ontario cause aesthetic and operational concerns, it also fails to meet the requirements established by the Ministry of the Environment (MOE), for the operation and closure of landfills, as specified in the "Certificate of Approval."

IV A Description of the "How-To" Manual

The purpose of the manual produced during this study is twofold:

- to assist the landfill owner/operator with the remediation of erosion on landfill sites through the establishment and management of vegetation; and
- to assist landfill designers with the prevention of erosion with a successful revegetation program.

The manual is simple and straightforward to use. It includes five main components:

- inventory of problem areas and existing conditions;
- examination of problems, proposing solutions;
- planning a revegetation program;
- implementation of the program; and
- follow-up care.

The manual is targeted towards an expected user group which includes landfill operators, owners, regulators, consultants, and academics.

Following is a brief overview of the main components of the manual:

a) Inventory of problem areas and existing conditions

In order to resolve erosion problems and establish or repair a vegetative cover, the problems need to be accurately assessed.

Two systems were prepared to help the operator gather and record the information required to address the problem. The first is the "Problem Evaluation Check Sheet." It records the physical characteristics of the problem areas of the landfill for later analysis, and is intended to be completed on-site. The second system is a key, which presents "either...or" descriptions of existing vegetation (or lack of). The key provides a decision path for the operator to follow through to problem headings which are addressed in the text.

By completing the Check Sheet (Figure 1) in the field during regular site inspections and for special problem solving investigations, these can provide a valuable history of the landfill.

The Check Sheet leads the investigator through an examination of the physical factors that influence growing conditions on the landfill slopes:

- slope length
- slope steepness
- erosion types (sheet, rill, and gully)
- soil texture
- organic matter
- compaction, and
- low soil moisture.

Verbal and/or visual assistance is provided with the Check Sheet and in the text of the manual to assist an untrained investigator in undertaking the investigation.

The second aid, the "Key to Problem Identification" (Figure 2), is intended to assist in identifying problems related to the growth of vegetation on a landfill. Copies of the key are to be taken into the field. For each problem area, the investigator can proceed through the "decision path" based on observations of the existing vegetation, or lack of it. Each decision path leads to a factor which may be related to the poor vegetative cover. Since more than one factor may be contributing to the poor growth, it is possible that several decision paths can be pursued, to determine all related causes. These decision path factors are referenced to the text of the manual, in which detailed descriptions can be found, along with solutions. As with any document regarding the landfill, it is recommended that completed keys be kept as a record of problem occurrence and remediation on the landfill.

b) Examination of potential problems/ proposed solutions

The causes of erosion on landfill slopes can often be interrelated, and therefore, confusing to interpret. The manual examines the causes individually, first describing the problem and how to recognize it, then outlining how to overcome it.

The problems examined are:

- excessive slope length and steepness;
- existing erosion;
- unfavourable soil characteristics:
 - excessive compaction;
 - high or low soil pH;
 - poor texture;
 - lack of organic matter;
 - absence of available nutrients;
 - toxic levels of nutrients and/or chemicals; and
 - lack of moisture, poor moisture capacity;
- leachate seeps;

FIGURE 1: PROBLEM EVALUATION CHECK SHEET

<p>1. <u>Instructions for Use</u></p> <p>Locate the problem areas on the landfill and sketch them on a copy of the site plan, an air photo, or on the attached diagram (Fig. 4). Using a check sheet for each problem area, check off the details that apply. Identify the different problem areas on the map as A, B, C, etc. and use the same coding on the check sheet.</p>	
<p>2. SITE: _____ DATE: _____ INSPECTOR: _____ WEATHER: _____</p>	
<p>3. Pace the distance from the toe to the top of slope, across the problem area. Take big steps, considering that each pace is 1 ± metre. More details can be found in Section 4.1.</p>	<p><u>SLOPE LENGTH</u> Long (150 to 300m) _____ Medium (60 to 150m) _____ Short (30 to 60m) _____ Very Short (0 to 30m) _____</p> <p>Check off correct range.</p>
<p>4. Have an assistant stand on the slope or use a stick about 2m in length which can be stuck into the ground. From a view point about 20 metres away on the same level, estimate the distance from the top of your assistant's head horizontally to the slope, using their height as a unit of measurement. This will give you the Vertical to Horizontal ratio of the slope, ie. one unit of height vertically = two units of height horizontally. Fig.5 shows other ways to measure slope steepness.</p>	<p><u>SLOPE STEEPNESS</u></p> <p>Check off closest range</p> <p><u>Vertical : Horizontal</u> 1 : 1 or Steeper _____ 1 : 2 _____ 1 : 3 _____ 1 : 4 or flatter _____</p>
<p>5. On bare ground portions of the slope, look for:</p> <p>° Upper layer of soil has washed away leaving exposed stones, sticks, debris.</p> <p>° Surface runoff has cut small channels 0 to 10cm in the cover materials.</p> <p>° Running water has cut one or more channels deeper than 10cm.</p> <p>One, two, or three erosion types may be present on the same problem area. Refer to Section 4.2 for more details.</p>	<p><u>EROSION TYPES</u></p> <p><u>SHEET EROSION:</u> Whole site* _____ Limited area* _____ Absent _____</p> <p><u>RILL EROSION:</u> Whole site* _____ Limited area* _____ Absent _____</p> <p><u>GULLY EROSION:</u> Present* _____ Absent _____</p> <p>*Be sure to sketch on plan.</p> <p>Check presence or absence of one or more erosion types, and note details such as length, width and depth.</p>

FIGURE 1: (Cont'd).

<p>6. Using the soil texture field tests described in Appendix C of the manual, determine the soil texture, or collect small samples in plastic lunch bags and bring them back to analyse when you can refer to the test instructions. Remember to identify where the sample was taken, using the coding for the problem areas. Refer to Section 4.3.3 for further details.</p>	<p><u>SOIL TEXTURE</u></p> <p>Sand _____</p> <p>Silt _____</p> <p>Clay _____</p> <p>Loam (topsoil) _____</p> <p>Check or describe appropriate texture _____</p>
<p>7. Look for dark soil colour with small bits of decaying leaves and roots. A small sample can be collected and labelled. When you get back, shake up the sample in a jar full of water. If there is organic matter in the sample, it will tend to float on the water in the jar. See also Section 4.3.4.</p>	<p><u>ORGANIC MATTER</u></p> <p>Present _____</p> <p>Absent _____</p> <p>Not Determined _____</p> <p>Check presence or absence _____</p>
<p>8. Observe whether the surface is smooth, hard, and/or difficult to push a shovel or stick into. This is further described in Section 4.3.1.</p>	<p><u>COMPACTION</u></p> <p>Yes (hard) _____</p> <p>No (softer) _____</p> <p>Not Determined _____</p>
<p>9. The presence of cracks, or soil blowing into drifts, usually indicates dry conditions. Refer to section 4.3.6. for description.</p>	<p><u>LOW SOIL MOISTURE</u></p> <p>Yes _____</p> <p>No _____</p> <p>Not Determined _____</p>

KEY TO PROBLEM IDENTIFICATION

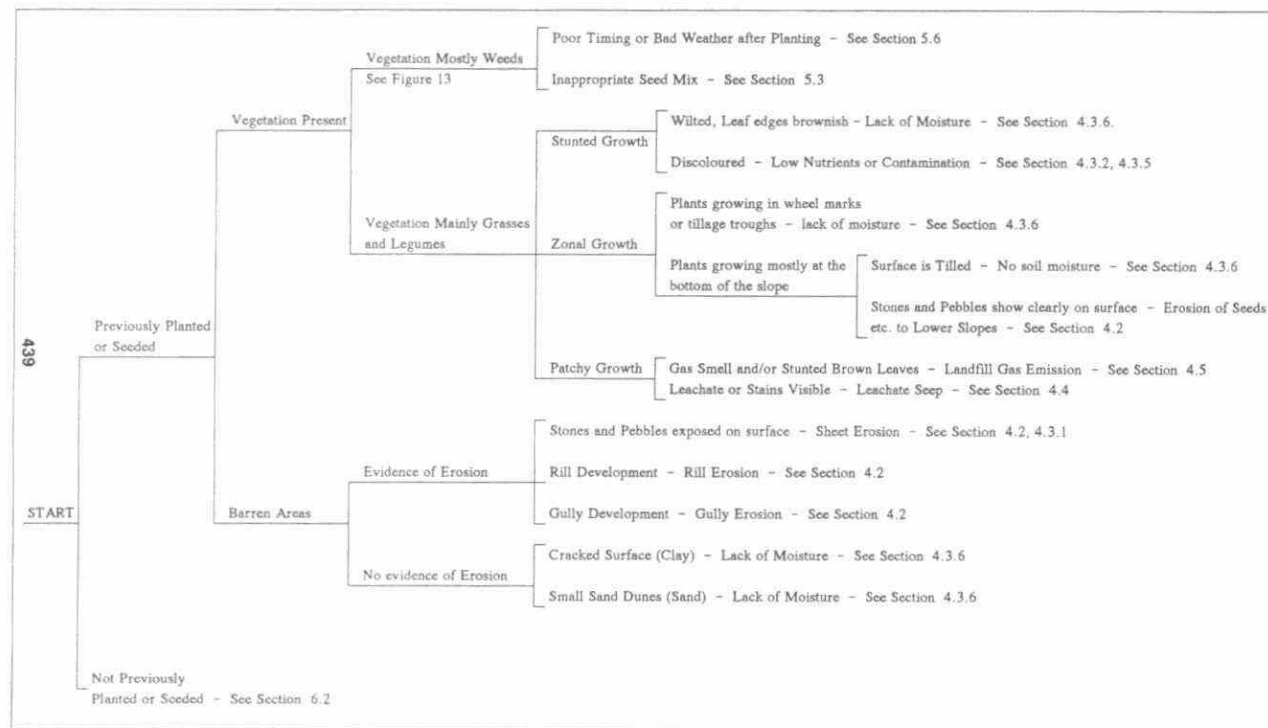


FIGURE 2: KEY TO PROBLEM IDENTIFICATION

- gas emissions; and
- poor or inappropriate existing vegetative cover.

Guidance is provided for undertaking some of the tests needed to evaluate the physical characteristics. In some cases, the manual specifies that the MOE be called for assistance, particularly where leachate and gas are involved, or if there are issues related to the Certificate of Approval.

c) Planning a program

Besides the obvious aesthetic requirement of revegetating a landfill site, a number of objectives were identified which should be satisfied by the vegetative cover. These are:

- to provide sufficient density of cover to reduce soil loss by rainfall impact;
- to provide sufficient density of shallow roots to bind the soil, especially at the surface, to resist the eroding forces of overland flowing water, and the cracking action of both the freeze-thaw cycle and the wet-dry cycle;
- to provide resistance or drag to flowing water and thus reduce its velocity and erosivity;
- to be self-sustaining, requiring low maintenance, with no root penetration of the cap; and
- to be capable of withstanding the intended end use.

In order to achieve these objectives, the characteristics of an ideal vegetative cover were identified:

- easy to establish, with good growth in the first growing season;
- sod forming with shallow, fibrous roots and multiple stem growth habit;
- self propagating by seeding, by root suckers, and/or perennial life cycle;
- low nutritional demands, tolerant of pH variation, ability to fix nitrogen, adaptable to variations in physical habitat; and
- reasonable tolerance to climatic extremes, especially drought tolerance.

Because of the great differences in climate and growing conditions in Ontario, the manual could not provide one recommended species or mix of species. Instead, the reader is provided with an understanding of how the ideal characteristics can be assembled from species which individually contribute to, and collectively satisfy the required cover characteristics, and are locally adapted and commercially available.

d) Implementation

A revegetation program is described, giving the landfill operator the correct sequence and timing of steps to be undertaken. These include the site inventory, soil testing, and the use and benefits of soil amendments, such as mulches, sewage sludge, lime and fertilizer. Guidelines on tillage, incorporation of soil amendments, and seeding techniques are provided. Approximate start-up and cut-off dates are provided for seeding in Northern, Southern, and Southwestern Ontario, with the best results usually obtained with spring seeding.

Instructions are given on how to obtain specialized supplies and seeds, soil tests, and professional and/or agency assistance.

e) Follow-up

The revegetation program may have involved a considerable expenditure of funds and resources. In order to obtain the maximum return from this expense, a commitment to follow-up care is essential.

Appropriate recommendations are provided on:

- vegetation monitoring;
- soils monitoring;
- maintenance;
- keeping records; and
- getting professional and/or technical assistance.

V Conclusion

This manual provides two methods of assessing site characteristics, with explanations of site factors, why they can be a problem, and how they can be improved. The manual does not provide cook-book solutions: each landfill site has unique physical characteristics related to it. Rather, this manual provides a means of assessing problems and determining possible causes. Upon this basis, improvements can be planned and implemented, as required, in order to establish an appropriate vegetative cover. The key points to include in a maintenance program are identified. Sources of assistance, materials, and information are provided to facilitate the implementation of a revegetation program on a particular site.

VI Acknowledgements

We wish to thank the Ontario Ministry of the Environment for funding this project. We are grateful for the help and technical assistance provided by the MOE members of the project steering committee, and by the staff of the Regional and District Offices of the MOE. A special thanks goes to the owners and operators of the many landfills which were visited.

QUANTIFICATION OF INFILTRATION THROUGH LANDFILL COVERS

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1.0 INTRODUCTION AND BACKGROUND

Decommissioned municipal solid waste sites often rely exclusively on the use of an earthen cap to restrict precipitation access to the underlying refuse material. While some infiltration is desirable for sustaining vegetative growth on the site, excess infiltration water which percolates beyond the soil storage zone and enters the buried waste can accumulate in the landfill, leach wastes into groundwater and enhance landfill subsidence. Consequently, the successful performance of the entire landfill can be very much a function of interactive processes operating to control water balance within the landfill cover (Nyhan, J.W., T.E. Hakonson and B.J. Drennon, 1990).

To provide a direct measurement of that portion of the infiltration water which passes through a landfill cap, it has been proposed that a field-scale lysimeter be installed in the landfill of concern. Previous studies have been undertaken to evaluate prototypes of an economical field-scale lysimeter suited to installation in a landfill cover (Ecologistics, 1990). The lysimeters installed and monitored in this study are a slightly modified version of the previously studied prototypes. The terms of the contract required the installation of a set of three (3) lysimeters under each of two (2) decommissioned landfill sites. The two landfill sites were to differ with respect to the textural characteristics of the final cover material applied. Once installed, a monthly volumetric measurement was to be made of the through-cover infiltration collected by each lysimeter. Trends in the rate of infiltration within the year were also to be collected. A set of in-field infiltration simulation experiments were to be undertaken to verify the satisfactory operation of the lysimeter. Finally, a mathematical simulation was to be performed to compare the results of existing soil water movement models with the measured values. This paper presents the interim findings of this study, which was still in progress at the time of writing.

2.0

DESCRIPTION OF LYSIMETERS

The lysimeters, based on the Kohnke, Dreibelbis and Davidson (1940) classification of lysimeters, can be described as filled-in lysimeters according to the principles used in their construction. They can also be described as free-drainage lysimeters, given that they drain freely to the atmosphere by accumulating infiltration water in a storage chamber below the soil mass. A cross-sectional representation of the lysimeters installed on both the Guelph and Barrie landfills is presented in Figure 1. The Guelph and Barrie site of significant features associated with the lysimeters include the use of 40 mil PVC liner to form the lysimeter walls, the use of 600 mm (24") Big "O" heavy duty perforated pipe to form the storage zone, the cutting of vertical slots in the monitoring well within the lysimeter's storage zone and the installation of the mastic and bentonite skirt at points susceptible to preferential flow.

The use of large diameter pipe in the storage zone provides ample storage capacity and facilitates the incorporation of a flexible storage zone datum. Later it was also discovered that the heavy duty pipe is capable of withstanding heavy machinery traffic during cover installation.

The slots in the monitoring well ensures rapid gas and water exchange between the monitoring well and the storage zone, simplifying the monthly task of pumping out the collected infiltration water.

3.0

DESCRIPTION OF INSTALLATION SITES

With logistical assistance received from the Ministry's assigned liaison officer, approval was obtained from the appropriate authorities to install the lysimeters on the Guelph and Barrie landfill sites. The Guelph site is located on the eastern outskirts of the city. A textural analysis revealed the Guelph cover to be a gravelly loam material (see Table 1). The cover was compacted during its installation. Measured densities associated with the completed cover ranged from 1.9 g/cm³ to 2.4 g/cm³. The Barrie site, located just west of the city off an access road that extends to Ferndale Avenue,

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uses locally available sand as the cover medium (see Table 1). Cover densities at Barrie are in the order of 1.8 g/cm^3 .

TABLE 1: TEXTURAL ANALYSIS OF THE CAP MATERIAL AT THE STUDY SITES

SITE	GR	VCS	CS	MS	FS	VFS	SAND	SILT	CLAY	TEXTURAL CLASS
	-----% by weight-----									
Guelph	37	3.7	5.0	7.8	19.9	13.7	50.1	40.4	9.6	gravelly loam
Barrie	0	2.5	10.8	36.6	37.9	6.1	93.9	3.6	2.4	sand

Timing of the lysimeter installation at both sites was such that it corresponded to the application of the final cover layer. For Guelph, this meant that, while the landfill cap itself had been applied at the time of lysimeter installation, the final loam cover or topsoil to support vegetative growth had not been added. A similar situation existed for the Barrie site. While a shallow covering was over the area of concern at the time of lysimeter installation, the final cover complex was not complete. With portions of the cover at both sites being applied following lysimeter installation, and with the ability of the lysimeters to withstand heavy equipment traffic, an improved situation existed to help ensure that similar cap and cover characteristics would be present over the installed lysimeters as are present within the surrounding monolith.

4.0 LYSIMETER INSTALLATION

Installation of the lysimeters at both sites was undertaken in September 1989. A rigid protocol was followed during construction. Installation began by digging a $4 \text{ m} \times 4 \text{ m}$ hole in the cap. Depth of the hole was dictated by the cover depth, for the lysimeters were installed in the zone of garbage at a depth which resulted in the side walls extending only 0.3 m ($1'$) into the overlying cap. As the cap was excavated, densities of the cap were taken using a neutron density probe at 15 cm ($6''$) intervals. These densities were used as a reference for restoring the cap as close as possible to its original condition when replacing the cap material over the lysimeter. All pertinent elevations

associated with the lysimeters such as the elevation of the patio stone at the base of the well were noted and related to a known benchmark.

Water level recorders including the shelter boxes were positioned over the monitoring well following lysimeter construction. As well, each lysimeter's storage zone was filled with water to test for leaks. No leaks were detected. The water was then pumped down to the pre-determined datum using a submersible pump attached to a metal stand. This stand, when set on the patio stone at the base of the monitoring well, positions the pump's intake at the storage zone's zero datum. The Guelph lysimeters were fully functional by December 1989, while the Barrie lysimeters were fully operational by January 1, 1990. The landfill covers themselves, however, were not complete. The final loam cover and seeding was completed at Guelph in April 1990. The bulk of the 5 foot deep sand cover over the installed lysimeter at Barrie was applied between November 1989 and June 1990. Final seeding has not been completed to date at Barrie.

5.0 MONITORING RESULTS

A comprehensive monitoring program has been implemented in an effort to fully assess lysimeter operation and accurately quantify the volumes of infiltration collected. At both sites, the through-cover infiltration water collected in the lysimeter storage zone is pumped out and measured volumetrically monthly. The same submersible pump and metal stand as was used in the initial establishment of the storage zone's datum is used to pump out the storage lysimeter to ensure a constant reference point throughout the study. Volumes pumped out to the end of August 1990 are presented graphically in Figures 2 and 3 for Guelph and Barrie respectively.

In addition to monthly volumetric measurements, the water level recorder, having a 32 day clock, records the water level within the storage zone. Its primary purpose is to identify trends in the relative timing or rate of accumulation of drainage water to the storage zone. Figures 4 and 5 present the recorded water level results. The data as presented has been adjusted to account for the porosity within the storage zone (95%) and to provide a continuous accumulative record of infiltration for the period. The y-axis scales on these graphs have been made identical to each other to visually assist in

FIGURE 2: MONTHLY VOLUMES OF PRECIPITATION AND THROUGH-COVER INFILTRATION - GUELPH LANDFILL

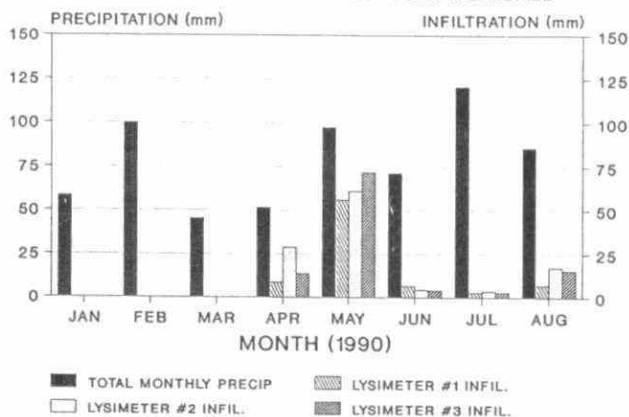


FIGURE 3: MONTHLY VOLUMES OF PRECIPITATION AND THROUGH-COVER INFILTRATION - BARRIE LANDFILL

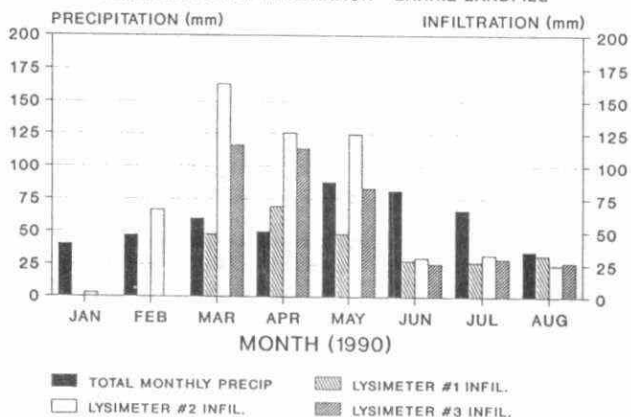


FIGURE 4
LYSIMETER MEASURED INFILTRATION
GUELPH SITE

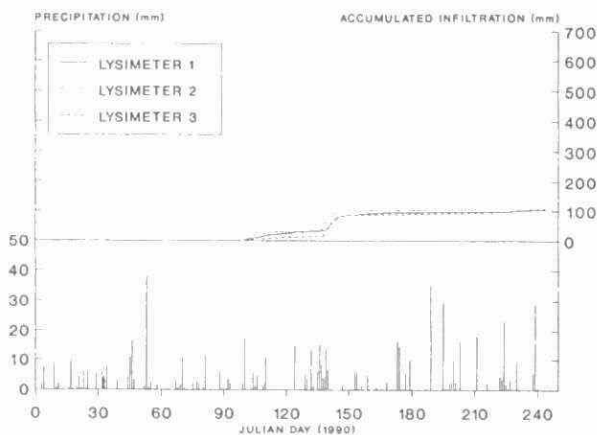
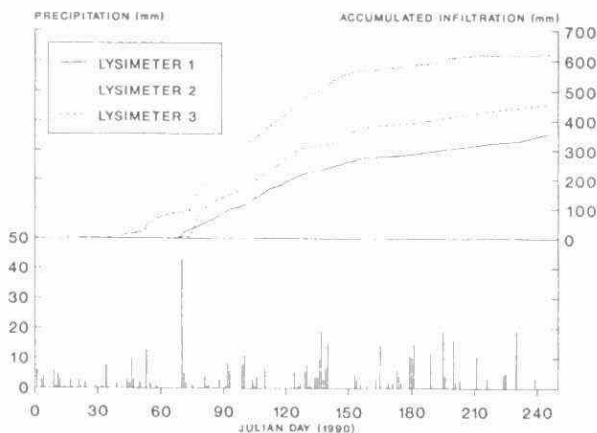


FIGURE 5
LYSIMETER MEASURED INFILTRATION
BARRIE SITE



comparing results between the Guelph and Barrie sites. Rainfall measured at a nearby weather station has also been added at the base of the graph to assist in identifying any possible relationships between precipitation and infiltration rates.

As seen from Figures 3 and 4, lysimeters at the Guelph landfill are giving nearly identical responses both in terms of infiltration volumes and the timing of infiltration. Barrie lysimeters show less similarity among each other. One main reason for this is the fact that the cover was still being applied on the Barrie site between January and June 1990. Consequently cover differences could easily have existed. Also, some of the cover was applied in the winter months when the opportunity existed for snow pack to be trapped in layers within the cover. This water would eventually drain during the spring thaw period. The graph in Figure 4 indicates that, while the Barrie lysimeters were collecting quite different levels of infiltration water until mid-April, trends since then have been quite similar. Time is required to see if this consistency among lysimeters continues now that the cover installation is complete.

Finally, note that to the end of August, infiltration levels through the Barrie cover have been on average 4.2 times higher, than for the same period at the Guelph site. Again, the delay in cover infiltration at the Barrie site is a factor here. If only data between May and August is considered, there is just a two-fold difference between the sites. The total infiltration measured at the Guelph site was on average 15% of the total precipitation that occurred in the same period. For Barrie, the average infiltration recorded was 73% of the total precipitation for the same period. Both sites are located on relatively flat areas of the landfill, encouraging water infiltration as opposed to water run-off.

Finally, a comparison was made between the direct volume measurements of infiltration and those indirect volume measurements made by converting changes in chart recorder readings to volumes. Field measurements and theoretical calculations have established the porosity of the lysimeter's storage zones to be approximately 95%. The surface area of the storage zone as constructed is known to be 3 m x 3 m. Chart recorder measurements are between 0.2% and 42% of the actual pumped values. This error is expected to originate to a certain extent from the inherent error associated with the chart recorders themselves which have a manufacturer's rated accuracy of ± 3 mm. In

this application such an inherent error is the equivalent of 26 litres of infiltration water. Errors can also arise from the monthly disturbance which occurs during chart changing. Regardless of the source, such a range in error does emphasize the need to measure lysimeter infiltration volumetrically if monthly readings within 10% of the actual levels are desired. Such a procedure is relatively convenient.

6.0 FIELD SIMULATION

A field scale infiltration simulation experiment was conducted at both the Barrie and Guelph sites to further verify the reliability of the lysimeters as a through-cover infiltration measurement tool. The experiment entailed installing a water-proof barrier around the perimeter of a 4 m x 4 m area within which the lysimeter to be tested was located. A simple irrigation system was installed inside the barriers to apply water at a very slow rate. A flowmeter recorded the volumes applied over the 16 m² area. This same area was completely covered with plastic to minimize evaporation/transpiration losses. Initial application rates were estimated using the cover's infiltration and percolation rates as measured by the Guelph infiltrometer and permeameter respectively.

To establish a consistency in initial conditions for the experiments to follow, the soil profile was wetted up beyond saturation and allowed to drain to field capacity. Once field capacity was reached, known volumes of water were applied gradually to the enclosed area.

The soil profile was assumed to have reached field capacity at the point where the water level recording chart was showing a horizontal line with time. Three separate applications were performed. The volumes subsequently collected in the lysimeters were compared with the theoretical volumes expected assuming no evaporation/transpiration losses. Results of the three runs on the Guelph site are shown in Table 2. The Barrie experiments were underway at the time of writing. Consequently, results were not available for printing. The Guelph data, however, instills a high degree of confidence in the ability of the installed lysimeters to measure through-cover infiltration with an average of 94% of the expected infiltration being captured under saturated or near saturated initial conditions over the three trials.

TABLE 2: RESULTS OF FIELD SCALE INFILTRATION EXPERIMENTS - GUELPH SITE

EXPERIMENT	THEORETICAL VOLUMES OF INFILTRATION WATER AVAILABLE TO BE CAPTURED	ACTUAL VOLUME CAPTURED	PERCENTAGE OF THEORETICAL
A	170	168	99
B	170	152	89
C	170	161	95

7.0 COMPUTER SIMULATION

The Hydrologic Evaluation of Landfill Performance (HELP) model, developed by the U.S. Environmental Protection Agency was employed in this project's modelling task. Authors of the model describe the HELP model as follows:

The (HELP) program was developed to facilitate rapid, economical estimation of the amounts of surface run-off, subsurface drainage, and leachate that may be expected to result from the operation of a wide variety of possible designs. The program models the effects of hydrologic processes including precipitation, surface storage, run-off, infiltration, percolation, evapotranspiration, soil moisture storage, and lateral drainage using a quasi-two-dimensional approach.

(Schroeder, P.R., A.C. Gibson and M.D. Smolen, 1983)

While the HELP model is no more complex than a computerized form of a manual tabulation of moisture balance, it combines accepted state-of-the-art mathematical models for computing an accurate water budget over a variety of climatic, soil and vegetative conditions. The purpose of applying this computer model to simulate operation of the lysimeters was to determine the degree of accuracy with which the HELP model could predict through-cover infiltration amounts.

Climatic input to the model included the 1990 precipitation data measured at the weather station closest to the site under analysis and the average monthly temperatures for 1990. Given that little vegetative cover had established on the site in 1990, bare ground conditions were assumed. The landfill cover profile overlying the lysimeters was also described in detail to assist in infiltration modelling. Guelph permeameter percolation readings were taken at each site and used as an estimate of each cover layer's saturated hydraulic conductivity.

Graphed results of the HELP run at each site are presented in Figures 6 and 7. They have been prepared in a format similar to the graphs of Figures 4 and 5 to assist in comparing computer simulated results with lysimeter measured data. The simulation results did not resemble the field measured levels of through-cover infiltration. For the January through August 1990 period, the model estimated 2.3 times more infiltration than the lysimeters measured at the Guelph site, while it predicted 5.7 times less infiltration than what was measured at Barrie. The predicted timing or rate of through-cover infiltration was also different from that shown on the lysimeter's well level charts. Possible explanations for the differences are numerous. For example, it was not possible to model the gradual application of cover material over the Barrie lysimeters. In taking permeameter readings on the Guelph site, the stoniness of the cover material and the slow rate of infiltration made it difficult to set-up and conduct the permeameter tests. Further analysis needs to be completed to determine whether the model can be refined or calibrated in a manner which will produce more representative results.

8.0 CONCLUSIONS

While this study is still in progress, observations to date are directing the study team to the following conclusions.

1. The lysimeters as installed are giving true readings of volumes of infiltration water passing through the overlying cover material.
2. Monthly volumetric readings are necessary for accurate determination of the amount of through-cover infiltration water collected.

FIGURE 6
INFILTRATION SIMULATION - GUELPH SITE

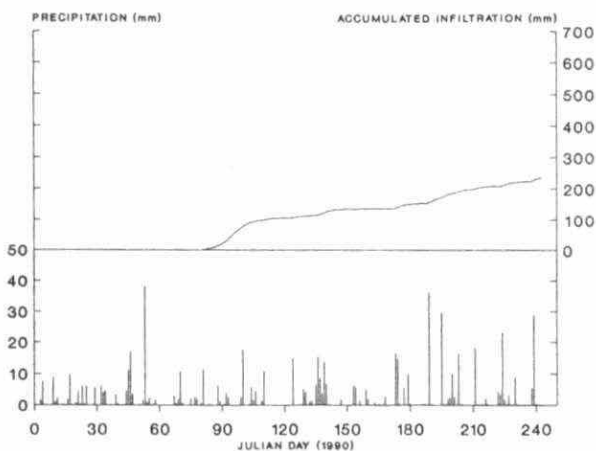
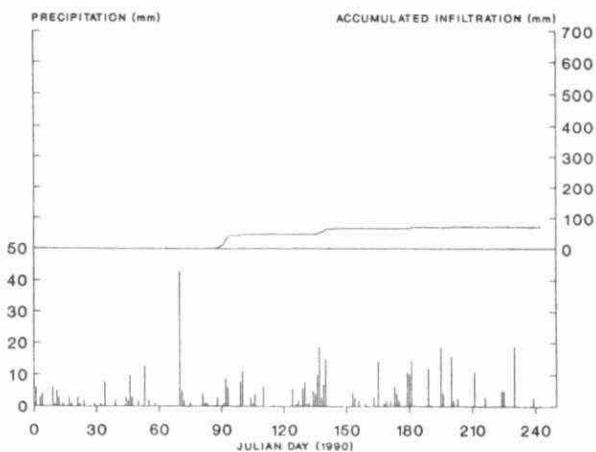


FIGURE 7
INFILTRATION SIMULATION - BARRIE SITE



3. The water level recorders can assist in identifying general trends with respect to the rate of through-cover infiltration within any given month.
4. Strict protocol must be followed during construction of the lysimeters to ensure proper installation and operation in the future.
5. Long-term monitoring of the installed lysimeters is necessary in order to assess the landfill cover's effectiveness in controlling through-cover infiltration.
6. Monthly monitoring of the lysimeters can be set-up to be a routine task.
7. The HELP model prediction of through-cover infiltration rates at both the Guelph and Barrie sites was poor. Refinements are needed for the model to produce desired results. Long-term data collected by installed lysimeters could provide data necessary to refine and calibrate an appropriate model.

REFERENCES

- Ecologistics Limited. 1990. Evaluation of Prototype Landfill Cover Lysimeters. Prepared for Waste Management Branch, Ontario Ministry of the Environment. Toronto.
- Kohnke, H., F.R. Dreibelbis and J.M. Davidson. 1940. A Survey and Discussion of Lysimeters and a Bibliography on their Construction and Performance. USDA Misc. Publ. No. 374, Washington, DC.
- Nyhan, J.W., T.F. Hakonson and B.J. Drennon. 1990. A Water Balance Study of Two Landfill Cover Designs for Semiarid Regions. *J. Environ. Qual.* 19:281-288.
- Schroeder, P.R., A.C. Gibson and M.D. Smolen. 1983. Hydrologic Evaluation of Landfill Performance (HELP) Model: Volume II, Documentation for Version 1. Draft Report. Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency. Cincinnati, OH.

Accurate Control Testing for Clay Liner Permeability
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ABSTRACT

Experience with commercial testing of clay liner samples for permeability evaluation has shown that standard laboratory permeability tests are subject to leakage problems which can effect the order of magnitude of the results. Furthermore, these tests typically take a week or more to complete and are, therefore, inadequate as field control tests. Physical modelling of various geo-environmental problems in a geotechnical centrifuge was initiated at Queen's University, Civil Engineering Department, in 1988 and it became apparent that the behaviour of clay liners was one of the problems for which centrifuge modelling was well suited. A dedicated 0.5m radius centrifuge was constructed, principally for long term behavioural studies of clay liners but which could also be used for control testing. This paper outlines recent research on the use of the 0.5m radius centrifuge for accurate control testing for clay liner permeability.

The test results are presented in three phases. The first phase used commercial kaolin clay samples prepared by consolidation into a specially designed permeability apparatus. This apparatus was designed for both bench and centrifuge use and allowed a direct comparison of the two methods. The centrifuge method was found to be efficient and reliable. The second phase of this research used a highly impervious compacted clay liner material in the Queen's University 3m radius geotechnical centrifuge. A methodology for accurate clay liner control testing in the centrifuge was developed. The third phase of testing was carried out to examine some longer term permeability variations in compacted liners as a preliminary evaluation of the usefulness of the 0.5m radius centrifuge for liner performance modelling.

The results of this of this research shows that a geotechnical centrifuge can be used to provide accurate control testing for clay liner permeability. The 0.5m radius centrifuge is relatively inexpensive, sufficiently mobile for field operations and can provide a one day liner permeability results in most cases.

INTRODUCTION

A number of researchers and consultants have had experience with clay liner permeability testing in the laboratory and in the field and the general consensus appears to be that liner leakage testing is wrought with problems (see for examples, Chapuis (1990a), (1990b); Quigley (1990); Mitchell (1990)).

Leakage errors in the testing apparatus and the long time required to obtain a satisfactory test result are the two major concerns in laboratory control testing. Field testing is not useful for hydraulic conductivities less than 10^{-9} m/s. A geotechnical centrifuge offers an alternative, relatively rapid and problem free method of evaluating clay liner leakage. A major problem with the specification of centrifuge models as a primary means of commercial liner permeability testing is the limited availability of geotechnical centrifuges. To alleviate this problem, the author has developed a 0.5m radius centrifuge for mobile testing. This paper presents the results of liner leakage testing carried out in this centrifuge.

The research is divided into three phases. Phase 1 research was conducted in the 0.5m radius centrifuge using a consolidated commercial white kaolin clay which was mixed at 100% water content (by dry weight) and consolidated into the permeability testing apparatus. The purpose of phase 1 research was to carry out a sufficient number of bench permeability and centrifuge permeability tests on saturated uniform clay to determine whether the two methods give similar results. Phase 2 research was carried out in the 3m radius centrifuge. The purpose of phase 2 research was to compare the results of triaxial permeability tests on a relatively impervious compacted clay to liner leakage model testing in a moderate sized geotechnical centrifuge. Phase 3 research used the same compacted clay at various moisture contents to carry out a preliminary evaluation of the 0.5m radius centrifuge for use in evaluation of the long term field performance of clay liners and was in progress at the time of writing of this paper.

A prototype clay liner will be overlain by landfill materials which may become saturated with liquids and, over a long period of time, liner leakage may occur. This worse case condition (or any other operational condition) can be modelled in a geotechnical centrifuge. Such centrifuges have been used world-wide for geotechnical physical model testing for the past two decades and are recently being used for research into other civil engineering problems, including environmental engineering problems. In its simplicity, the centrifuge simulates gravitational forces by induced centripetal forces so that a small model may experience prototype stresses and prototype flow and fracture phenomenon. The induced simulated gravity is given by

$$\lambda = r\omega^2/g \quad (1)$$

where λ is the liner scale factor, r and ω are the centrifuge radius and speed, respectively, and g is the earth's gravitational constant. For a detailed review of geotechnical centrifuge applications, the reader is referred to Schofield (1980).

The total and effective stresses at all similar points in the model and prototype liners will be identical but the hydraulic gradient across the model liner will be increased by the modelling scale factor. If, for example, a prototype liner of 2m thickness is supporting an overlying 20m head of water, the hydraulic gradient is 10. If a model is designed at a scale factor of $\lambda = 35$, the 57mm thick model would then have an hydraulic gradient of 350 and one day of testing in the centrifuge at $\lambda = 35$ would produce λ^2 days or 3.35 years of prototype per unit area leakage. In fine grained soils Darcy's Law is considered to be applicable over a wide range of gradients (Goodings, 1985).

TEST METHODS

Most methods of measuring permeability of soils involve potential variations and errors. Variations develop in the preparation of most soil samples and errors result from equipment leakages. To carry out a meaningful statistical evaluation of the centrifuge method of clay liner permeability testing it was necessary to develop a leak-proof apparatus in which both bench and centrifuge permeability tests could be carried out under similar conditions on the same samples of a uniform and reproducible clay soil. A saturated consolidated commercial kaolin clay was selected, due to both uniformity and order of magnitude of permeability, as the most suitable clay material. Clay samples for bench permeability testing were preconsolidated to 250 kPa. During a test the sample is surrounded by a silicon rubber membrane and a silicon oil pressure seal of 100 kPa to prevent any possibility of leakage. The hydraulic head applied across the 50mm thick sample was 50 kPa, creating a nominal gradient of 102 and a seepage pressure of about 50 kPa. Over a three month test period a total of 16 independent tests were carried out.

The phase 1 samples remained in the permeability apparatus during transfer from bench to centrifuge and the boundary stress conditions were similar in each test. The centrifuge induced hydraulic gradient across the sample, however, is 163 and the seepage pressure is 80 kPa. Thus the flow rate in the centrifuge is about 1.6 times faster than in the bench test. Never-the-less, the test conditions in both methods are considered closely similar. The test time in the centrifuge was about 3 to 4 hours compared with 6 to 8 hours in the bench tests. The mass of water in the catchment container was measured after one hour of spinning and again at the end of the test. The one hour check point served the purpose of determining whether any consolidation or other "initial phenomenon" were taking place in the centrifuge. In most cases the N hour mass transfer was very close to N times the one hour mass transfer.

In order to compare centrifuge leakage models with triaxial permeability testing, phase 2 testing included double membrane, back pressured triaxial permeability tests on a local illite clay material. A standard Proctor compaction test on this clay gave a maximum dry density of 1.37 g/cc at an optimum water content of 35.5%. The material was stored at this water content and was subjected to standard Proctor compaction to form samples which were subsequently trimmed for permeability testing. After testing the used materials were remixed with the original batch and stored for further testing. Two triaxial cells with back pressured systems (Bishop & Henkel, 1962) were newly assembled, platens were polished and leakage testing of the systems was carried out before the permeability testing was begun. In total, six acceptable tests were carried out over a two month period. This is an average of less than two tests per cell-month, mainly because the system required considerable attention and repair during that time period.

The Queen's 3m radius centrifuge is described by Mitchell (1986) and Figure 1 shows the apparatus developed for liner modelling. The liner model is nominally 50mm thick, and is trimmed to fit snugly in a double thickness membrane encased perspex ring. The overlying landfill materials are simulated by a known mass of lead shot overlying a porous plastic disk placed on the top of the liner model. Double thickness filter paper and a porous stone underly the model. Stand pipe arrangements are used to create the water pressure and the confining pressure, which both increase as the simulated gravitational force increases in flight. The confining pressure is maintained at 35 kPa above the water pressure in order to effect a tight contact between the liner model and the rubber membrane. Phase 2 testing was carried out at a scale factor of $\lambda = 35$ with the model representing a 1.7m thick prototype liner. The centrifuge induced hydraulic gradient was 420.

TEST RESULTS

The phase 1 test data is summarized on Table 1. It can be noted that the earliest samples, KP 1 to 4 showed relatively high permeabilities because the preconsolidation pressure was below the desired level of 250 kPa. These samples also gave apparent permeabilities from the centrifuge method which are 1.3 to 1.8 times higher than in the bench test. This is due, no doubt, to consolidation under the simulated gravitational stresses induced in the centrifuge. In this case the effective vertical stress is given by

$$\sigma_v^1 = (z\rho\lambda + iz\rho\omega)g \quad (2)$$

where z is the sample thickness, g is the gravitational constant, ρ is the sample density, λ is the scale factor (a/g), i is the induced hydraulic gradient and $\rho\omega$ is the

density of water

The value of σ_v^1 in the centrifuge model is then calculated to be about 120 kPa. The applied confining stress in the early test was 80 kPa and this would also have contributed to sample consolidation. Subsequent samples were all consolidated to a vertical effective stress, σ_v^1 , of 250 kPa and a confining stress of 100 kPa was used in subsequent tests. It can be seen from Table 1 that subsequent tests (samples KP5 to KP16) provided a fairly consistent set of permeability data. All test data was plotted to obtain the best fit slope of the volume change vs. time line from which the permeability was calculated. The data on Table 1 clearly shows that the 0.5m centrifuge can be used effectively and efficiently to evaluate the permeability coefficient (hydraulic conductivity) of a consolidated clay material.

The results of the phase 2 triaxial permeability testing are contained in Table 2. All samples for which results are tabulated were back pressured to 300 kPa and subjected to an hydraulic gradient of 40. This laboratory testing was carried out at 20°C. From the data it is estimated that the mean permeability value is close to 2.3×10^{-11} m/s with individual test values from 0.3 to 1.3 times the average value. For material evaluation, this data seems reasonably acceptable although the scatter is quite significant.

Phase 2 liner leakage model tests were carried out over periods varying from five hours to ten hours. During some tests the centrifuge was stopped every two hours to check the mass transfer of water by weighing the catchment container (± 0.005 g). Mass transfer quantities were in the order of 0.1 g/hr and the variance found during the two hour interval tests was generally less than 20%. Table 3 shows the data from all of the centrifuge liner leakage model tests carried out. The average leakage rate, from the data on Table 3, is 0.10 cc/hr with a maximum individual test variance of 20%. The water temperature in the centrifuge liner model apparatus increased 0.5°C above the constant laboratory temperatures of 20°C during the first hour or two of spinning at 108 RPM and then remained constant throughout the remainder of the test. The calculated coefficient of permeability, from the average leakage rate is 2.2×10^{-11} m/s. With standard temperature correction, the hydraulic conductivity is estimated to be 2.0×10^{-11} m/s. This value is remarkably close to the average obtained from the triaxial permeability testing but the centrifuge data is more consistent than the triaxial data. This provides some confidence in individual liner control tests carried out by centrifuge modelling.

The compacted liner samples used in phase 2 are more dense than the consolidated samples of phase 1 such that there would be no consolidation during centrifuge liner leakage model tests on compacted samples.

CONCLUSIONS AND RECOMMENDATIONS

From the test data reported, it is concluded the centrifuge model liner leakage testing gives more consistent results for a low permeability compacted soil than triaxial permeability testing. The latter testing is subject to both technical difficulties and leakage risks. It is concluded that a centrifuge liner leakage model can provide realistic liner performance evaluation and that the hydraulic conductivity obtained from such a model will be closely similar to the average values found from good quality triaxial permeability testing.

The main advantages of centrifuge liner leakage models over any permeability tests are:

- (1) Realistic modelling of stress conditions in the liner.
- (2) Elimination of leakage provides more consistent results.
- (3) Elimination of induced hydraulic fracturing.
- (4) Rapid evaluation for construction control testing.
- (5) Greater potential for modelling liner performance.

A complete specification for accurate control testing for clay liner permeability using the 0.5m radius centrifuge has been prepared. This machine is relatively inexpensive and provides a one day control test result in most cases. It is recommended that the centrifuge method of liner leakage control testing be approved for use on liner clay liner construction projects. Further research on liner performance modelling is also recommended.

ACKNOWLEDGEMENTS

Phase 1 and Phase 3 tests, as reported herein, were carried out with the financial support of an Ontario Ministry of the Environment contract (Project 506C). The Author also acknowledges the support of the Natural Sciences and Engineering Research Council of Canada for financial support of centrifuge modelling and, in particular, support for the phase 2 testing program.

REFERENCES

- Bishop, A.W. and Henkel, D.J. (1962). The Measurement of Soil Properties in the Triaxial Test (2nd Edition). Edward Arnold Ltd., London.
- Chapuis, R.P. (1990a). Sand - Bentonite Liners: Predicting Permeability from Laboratory Tests. Canadian Geotechnical Journal 27:1:24-57.
- Chapuis, R.P. (1990b). Sand - Bentonite Liners: Field Control Methods. Canadian Geotechnical Journal 27:2:216-223.

Goodings, D.J. (1985). Relationships for Modelling Water Effects in Geotechnical Centrifuge Models. In Applications of Centrifuge Modelling to Geotechnical Design, W.H. Craig, Editor. Balkema, pp. 1-24.

Mitchell, R.J. (1986). Centrifuge Model Tests on Backfill Stability. Canadian Geotechnical Journal 23:3:341-345.

Mitchell, R.J. (1990). Clay Liner Leakage Evaluation. Proceedings 43rd Canadian Geotechnical Conference, Quebec City, October, 1990 (4 pages).

Schofield, A.N. (1980). Cambridge Geotechnical Centrifuge Operations: Twentieth Rankine Lecture. Geotechnique 30:3:227-268.

Quigley, R.M. (1990). Caly Barriers for Mitigation of Contaminant Impact. Course Notes, Geotechnical Research Centre, University of Western Ontario, Vol. 2, pp 1-31, April 1990.

Sample No	Saturated density g/cc	BENCH TEST		CENTRIFUGE TEST	
		test time min.	hydraulic conductivity m/s x 10 ⁻⁹	test time min.	hydraulic conductivity m/s x 10 ⁻⁹
KP1	1.82	450	1.46	180	2.65
KP2	1.81	450	1.65	180	3.05
KP3	1.84	810	1.10	210	1.58
KP4	1.88	810	1.35	210	1.73
KP5	1.91	480	1.12	240	1.13
KP6	1.90	480	1.05	240	1.14
KP7	1.95	420	0.96	180	1.06
KP8	1.87	420	1.27	180	1.27
KP9	1.90	420	1.27	180	1.37
KP10	1.86	420	1.18	180	1.19
KP11	1.87	450	1.21	240	1.30
KP12	1.92	450	1.10	240	1.21
KP13	1.88	1100	1.28	180	1.23
KP14	1.94	1100	1.11	180	1.12
KP15	1.86	465	1.15	180	1.24
KP16	1.89	465	1.15	180	1.11

Table 1 - Phase 1 Test Results Summary

Test No	Test Time (days)	hydraulic conductivity $\text{m/s} \times 10^{-11}$
LPTX2	9	3.3
LPTX3	8	0.8
LPTX4	7	0.9
LPTX5	8	5.3
LPTX6	12	1.1

Table 2 - Phase 2 Triaxial Tests

Model No	Run time (hrs)	Hydraulic conductivity $(\text{m/s} \times 10^{-11})$
LPCM1	5	2.0
LPCM2	7	2.2
LPCM3	8	2.2
LPCM4	6	2.6
LPCM5	10	1.8
LPCM6	8	2.5

Table 3 - Phase 2 Centrifuge Models

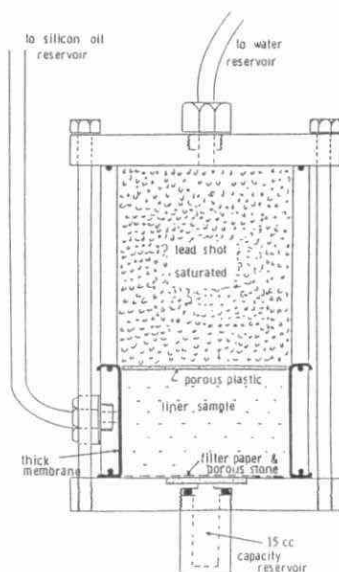


Figure 1 - Drawing of the Centrifuge Liner Model Apparatus

Field Demonstration of Membrane Technology for Treatment of Landfill Leachate

by

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Abstract

Landfill leachates commonly contain a wide spectrum of organic and inorganic contaminants which may pose a threat to surface or groundwater use. A variety of treatment processes have been considered and evaluated for the treatment of landfill leachates, including both biological and physical/chemical treatment processes. The objective of this study was to provide a technical and economic assessment of a membrane based process for treatment of landfill leachate. A two-stage process incorporating precipitation/microfiltration to remove heavy metals and suspended solids, followed by reverse osmosis to remove residual organics and dissolved metals was developed and tested by Zenon at pilot scale for treatment of a low strength landfill leachate.

Results of the field testing program demonstrated that the microfiltration system achieved stable flux rates ranging from 92 to 132 litres/meter²/hr. A reverse osmosis system was used to further treat the MF permeate, and stable fluxes of approximately 32 litres/meter²/hr were obtained with the RO. Overall process removals for key contaminants of concern were generally over 90%, at waste volume reductions of 75-80%.

A comparison of the costs of the developed process with alternative conventional processes was conducted and indicated that a treatment process incorporating conventional precipitation/clarification and reverse osmosis can provide a cost effective alternative to biological treatment at some sites, and may be particularly suitable for application where treatment is required prior to spray irrigation or recirculation. In order to further evaluate potential applications of this technology, a pilot scale testing program should be undertaken to determine the performance and cost of membrane treatment for higher strength landfill leachates.

Introduction and Background

Landfill leachates are complex wastes containing a variety of both organic and inorganic contaminants. The quality of leachate varies substantially between sites, and is affected by the type of waste disposed, site specific hydrogeology, age of the landfill, and the biodegradability of the different organic contaminants present. As a result, a variety of treatment processes have been considered and evaluated for treatment of landfill leachate. Biological treatment has been used reliably and effectively however, leachates which have a larger proportion of higher molecular weight refractory organic contaminants, or high levels of toxic metals, may not be readily amenable to biological treatment. Research undertaken over the last few years has demonstrated the technical feasibility of reverse osmosis and other membrane processes in various capacities for the treatment of industrial wastes, and recently, for application in the treatment of landfill leachate.

Membrane Separation

Membrane based systems hold significant potential for treatment of such leachates and may be incorporated with other pre and post-treatment processes, including biological or physical/chemical treatment, as appropriate. Membrane separation is referred to as a cross-flow filtration process since the flow of feed is across the membrane surface. The three main membrane filtration processes (microfiltration, ultrafiltration and reverse osmosis) are all based upon flow through a semi-permeable membrane where pressure is the driving force, however they each have different membrane characteristics, separation principles, and operating conditions.

In the microfiltration process, the filtration surface is a strong polymeric membrane cast on the inside surface of a support tube, as shown in Figure 1. Feed is pumped at relatively low pressures (up to 60 psi) through the membrane tube. The water and dissolved components pass through the membrane as clean filtrate or permeate, while suspended solids and fine particulate material are retained by the membrane and remain with the feed. The feed becomes more concentrated as it flows down the membrane tube. Turbulence from the flow keeps the filtration surface clear of any build up of contaminants which would reduce the filtration or permeate rate. Microfiltration (MF) processes have pore diameters of 0.08 to 1.0 microns, and effectively remove suspended solids which are not easily settled. MF has been applied to the treatment of contaminated wastewaters as the solids removal step after chemical precipitation of toxic metals.

Ultrafiltration processes (UF) operate in a smaller filtration range, with pore diameters of 0.002 to 0.1 microns, and are commonly used for the concentration of wastewater containing emulsified oils or large molecular weight organic contaminants.

Finally, reverse osmosis (RO) processes have a filtration range of less than 0.002 microns and are used for the removal of dissolved solids (salts) and dissolved organic contaminants. In reverse osmosis the contaminated water is passed under pressures from 200 to 1,000 psi across a membrane surface. Pure water preferentially permeates the membrane, leaving the suspended and dissolved contaminants concentrated on the feed side. Rejection levels are dependent on the size and charge of the dissolved molecule with larger molecules and higher charge being more highly rejected.

Process Development

In 1988, bench scale work was undertaken by Zenon on behalf of the Ontario Ministry of the Environment to evaluate the potential for reverse osmosis as part of a complete system for the treatment of landfill leachate. Results of the bench scale study confirmed the technical feasibility of the two stage membrane-based process (Krug and McDougall, 1988).

Figure 2 presents a schematic of the process developed. The first stage involves pH adjustment and precipitation of heavy metals and hardness, followed by microfiltration. The potential benefits of the process over conventional precipitation and settling processes include the ability of the process to completely remove toxic heavy metals, and remain insensitive to upset conditions and sludge settling characteristics. A membrane process is also compact in size relative to conventional clarifiers. The resulting primarily inorganic sludge, generated as concentrate from the MF, would be dewatered in a plate and frame filter press and the filter cake disposed appropriately.

The MF permeate containing dissolved organics and inorganics would then be subjected

to final polishing by reverse osmosis to produce a high quality effluent. Reverse osmosis will serve to reduce hydraulic loading on any downstream treatment processes such as spray irrigation, reduce volume for off-site disposal, and generate a high quality product stream suitable for surface discharge. The concentrate from the RO process, containing primarily organic components which were not removed in the first stage precipitation/microfiltration process, can be disposed of off site, used for spray irrigation, or recycled to the landfill site itself.

This process was recently tested at pilot scale at a landfill site in Ontario. The objectives of the field program were to continue the development of a membrane based process for treatment of landfill leachate by conducting a pilot scale field demonstration, and to provide an assessment of the technical effectiveness and cost of the process based on pilot scale data.

Field Testing Program

Site Description

The Muskoka Lakes Sanitary Landfill site was selected for pilot scale evaluation based on leachate quality and quantity, treatment requirements, as well as site access and availability of support services.

The leachate at the site is presently collected in a trench which is situated downslope of the site. It is collected in a sump, pumped to two settling lagoons where a limited degree of natural aeration and biodegradation occurs, and then pumped to a network of spray nozzles for land distribution over a forested area. The volume of leachate requiring treatment is expected to exceed the capacity of the current spray irrigation system and researchers have found that pretreatment is necessary to prevent damage to vegetation (McBride et. al., 1988). A process capable of reducing both chemical concentration and hydraulic loading would therefore be of benefit at such sites.

The primary contaminants of concern in this leachate are Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), iron, manganese and solids. The leachate was relatively dilute, with TOC and BOD levels at approximately 250 mg/L, COD at 500 mg/L, and Iron at 150 mg/L. Key volatile organic contaminants are shown to be toluene, with low levels of benzene and ethylbenzene. Low levels of several chlorinated solvents were also detected, including 1,1-dichloroethane, and 1,2-dichloroethane.

System Design

The pilot scale treatment system was designed with the objective of maximizing performance and effluent quality, in order to generate an effluent suitable for surface discharge.

The microfiltration test unit consisted of a polyethylene tank, a single stage centrifugal pump, two tubular membrane test modules (operated in parallel), a central control panel, a clean-in-place tank, and associated tubing, valves and pressure gauges. The total feed flow rate was 40 gpm, operated at 60 psi. The membranes used for the field testing program were Zenon AST membranes, which have a neutral charge and a molecular weight cut off of approximately 200,000. The microfiltration membrane module contains eight tubes in an internal series flow configuration. Each tube is 2.1 cm (0.84") in diameter and approximately 1,956 cm (77") in length, for a total surface area per module of 0.98 m² (10.5 ft²). The high turbulence in the large diameter membrane tubes allows the membranes to tolerate high levels of suspended

solids and maintain consistently high permeate rates.

The MF permeate was then fed into the RO system. The reverse osmosis test system consisted of a 650 L polyethylene tank, a feed pump, a process pump, one 4" X 40" Filmtec FT 30 spiral membrane module, a central control panel, a clean-in-place tank, interconnecting piping, valves and pressure gauges. The feed was pumped at a rate of 5 gpm at 400 psig.

Results and Discussion

The microfiltration/reverse osmosis pilot system was installed on-site in September, 1989, and performance was evaluated through a series of twelve tests over an eight week period.

Reverse osmosis treatment processes generally require pretreatment to remove particles larger than 5 μm , and to remove and feed components which could potentially foul, damage or scale the membrane units. The impact of complex wastes on membrane performance is difficult to predict and must usually be determined based on laboratory and/or field testing. Prior to the field program, a short series of bench scale tests were conducted to confirm the pretreatment requirements. Suspended solids, iron and calcium salts can foul RO membranes, thus chemical precipitation is required prior to the microfiltration step to reduce the concentration of the contaminants in the MF permeate. Both sodium hydroxide and lime were evaluated to precipitate metals, and lime precipitation was selected for the field trials based on superior membrane flux.

The pilot system was designed and operated in a batch treatment mode. Stability tests were initially conducted to establish baseline fluxes upon exposure to the feed. A series of concentration tests were then conducted to establish performance at various concentration factors. Since volume reduction was limited by batch size due to tank and pump configuration, several tests were conducted to treat a larger batch and thereby more closely simulate continuous operation. This was achieved by reducing the feed volume to a desired concentration level, and then adding fresh feed to top up the tank. Chemical dosages were also optimized during the study. The final two runs were conducted under optimized treatment conditions and represent the best performance achieved during the study.

Microfiltration Performance

The permeate rate, or flux, and the extent to which the feed can be concentrated without fouling the membrane, are important performance criteria. The microfiltration tests demonstrated that high and stable flux rates, ranging from 92 to 123 litres/cubic meter/hour (LMH), can be maintained using raw leachate treated with lime, even at volume reductions greater than 90%. This represents a concentration factor of ten, since 90% of the volume in the feed was recovered as treated permeate. Figure 3 presents the flux, or permeate rate, obtained during the course of one of the final optimized runs. The operating conditions of volume reduction and operating temperature are presented to show how the permeate rates were affected by these variables. In this run, lime was added to raise the pH of the feed from approximately 6 to 8. As expected, the flux was affected by operating temperature but the effect of increasing volume reduction was generally quite small.

The results of chemical analyses for the final optimization test are given in Table 1. In general, the results confirmed that all suspended solids and metals were effectively removed by the MF. Solids and metals, specifically iron, were removed to at or near detection limits. The

consistent removal of iron is important for downstream RO operation. Calcium, which was contributed mostly by the lime used to raise pH was reduced by approximately 70%. As expected, very limited reduction in organics was observed since most organic contaminants would be small enough to pass through the MF membrane.

The permeate, having no suspended matter and containing only dissolved organics and inorganics was suitable for further polishing by RO.

Reverse Osmosis Performance

The pH of the MF permeate was adjusted to approximately 6 by the addition of HCl to reduce the potential for calcium carbonate scale formation during reverse osmosis concentration. Figure 4 presents the permeate rates obtained during the final optimization run. Rates were stable at approximately 32 LMH at volume reductions over 80%. However, at concentration levels over 75%, soda ash must be used along with the lime prior to MF in order to further reduce tendency for scale formation in the RO system.

Analytical data are presented in Table 1, along with overall process rejections. The results confirm that the RO process is capable of removing a very high percentage of the organics present. Values for TOC were reduced from an average of 200 mg/L by 94% down to an average of 12 mg/L. Values for BOD were reduced from an average of 230 mg/L by 93% down to 14 - 15 mg/L. This high quality of RO treated water satisfies the general surface discharge guideline of 25 mg/L BOD. Toluene which was present at approximately 120 µg/l in the raw feed was reduced by about 50% across the MF, with a further reduction down to 14 µg/L across the RO. Total dissolved solids were reduced from 600 mg/L to about 130 mg/L in the final effluent.

The RO permeate met most criteria for surface water quality, as well as key drinking water quality parameters, and would therefore likely be suitable for surface discharge.

Economic Assessment

The field test results confirmed that the process was technically effective. An economic assessment was then carried out in an attempt to estimate the cost of a membrane based process compared with other process trains capable of achieving similar effluent quality. Capital and operating costs were developed for each of three different treatment process, with capacities ranging from 55 to 165 m³/day. Equipment costs are based on manufacturers selling price for packaged skid-mounted system components. The installed costs include all costs associated with the facilities including foundations, instruments, piping, insulation, buildings, and services, as well as construction and field expenses, engineering and contractors fees. For the purpose of this cost comparison it has been assumed that the dewatered solids generated from both the precipitation/MF and precipitation/clarification processes can be disposed at the landfill site at a nominal cost.

The processes considered in the economic assessment are as follows:

- 1) precipitation/MF for metals removal followed by reverse osmosis to reduce the volume of leachate water, and irrigation of the concentrated organic stream for final disposal on-site
- 2) precipitation/clarification and sand filtration for metals removal followed by RO and irrigation on-site

3) precipitation/clarification and sand filtration for metals removal followed by rotating biological contactor to degrade the organic contaminants present.

Processes 1 and 2 above are based on the assumption that the organic concentrate can be disposed of by spray irrigation or other means at the landfill site. If on-site disposal is not feasible, the cost of hauling or disposal of residue would be added to the the first two processes, and would be dependent on distances and associated disposal costs.

The capital and operating cost comparison of the three treatment trains indicated that the cost for the treatment process tested during the field evaluation (Process 1) was the highest of the three alternatives considered, at \$4.66 per thousand liters for a system capable of treating 165 m³/day. This is mainly due to the fact that costs for the precipitation/MF process, which are based on fluxes achieved during the test runs, proved to be somewhat higher than for conventional precipitation/clarification for removal of metals and suspended solids. The cost-competitiveness of the MF process could be improved if the capacity performance or flux of the membranes can be improved, if the cost for the membranes can be reduced or, if non cost issues, such as assured removal of all suspended solids or limited site space dominate the evaluation.

Process 2, where conventional precipitation/ clarification is used as the metals removal step and reverse osmosis is used for organics removal, was the least expensive option, at \$3.23 per thousand liters.

Process 3 was based on conventional precipitation clarification followed by a Rotating Biological Contactor for degradation of organics was estimated to cost approximately \$3.68 per thousand liters.

Conclusions and Recommendations

The results of the field testing program indicated that the precipitation/microfiltration and reverse osmosis process was successful in achieving surface water quality and drinking water quality objectives for all inorganic parameters of concern. Organic parameters were at or near drinking water quality guidelines.

The first stage precipitation/microfiltration process was capable of effectively removing suspended solids and metals from the raw leachate. The permeate contained only dissolved organics and inorganics and was suitable for further polishing by RO. The second stage reverse osmosis system was successful in removing a high percentage of the organic contaminants present as TOC, COD, and BOD, as well as dissolved solids, from the MF permeate. The RO was capable of achieving 80% volume reduction, and generated a high quality final process effluent and a concentrated, primarily organic residue.

A cost comparison of three alternative treatment trains indicated that conventional precipitation/clarification was less expensive than precipitation/microfiltration as a form of pretreatment prior to RO for this application. The costs of a treatment process using conventional precipitation/clarification for metals removal followed by reverse osmosis compare favourably with the costs for precipitation followed by biological treatment in the form of an RBC, where organic concentrate can be disposed on site. The process may be particularly suitable for application at sites where recirculation or spray irrigation practices are limited by excessive hydraulic loading or toxic metals. This option may also have an advantage over biological treatment in applications where immediate start-up of a treatment process is required

because it does not require establishment of an acclimated microbial population. Further testing of this process at larger scale should be undertaken to evaluate performance and treatment costs on higher strength landfill leachates.

Acknowledgement

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References

Krug T. and McDougall, S., 1988. "Preliminary Assessment of a Microfiltration/Reverse Osmosis Process for the Treatment of Landfill Leachate." Proceedings - Environment Ontario Technology Transfer Conference, Toronto, Ontario, November 28-29, 1988.

McBride, R.A., Gordon, A. M. and Groenevelt, P.H., 1988. "Treatment of Landfill Leachate by Spray Irrigation (Muskoka Lakes), Ontario Ministry of the Environment, Research Advisory Committee, Project No. 244-RR.

Figure 1
Cross Flow Filtration

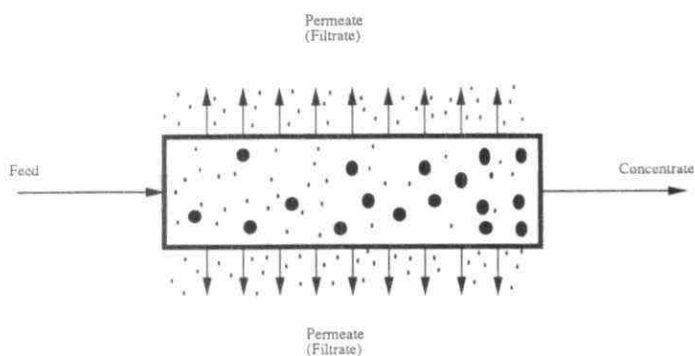


Figure 2
Process Schematic for
Treatment of Landfill Leachate

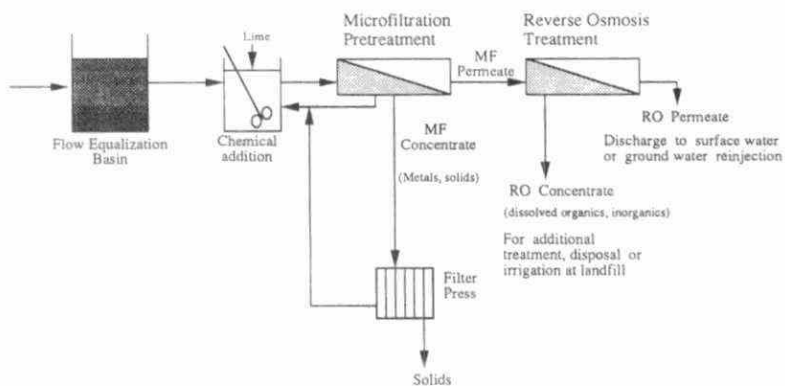


Figure 3
Microfiltration System Operation - Pilot Test # 11

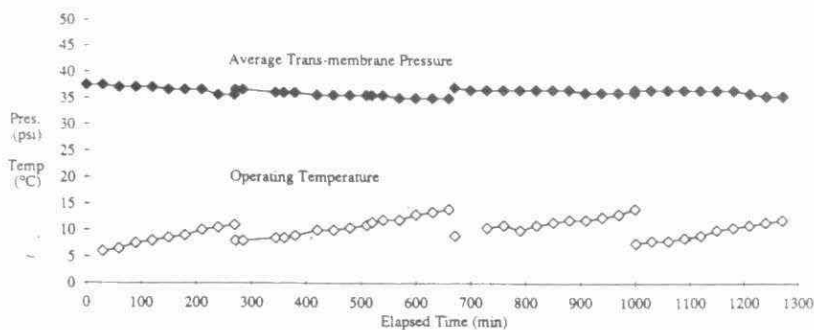
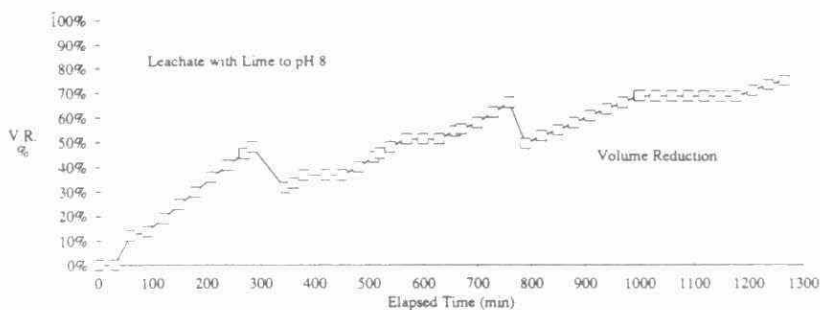
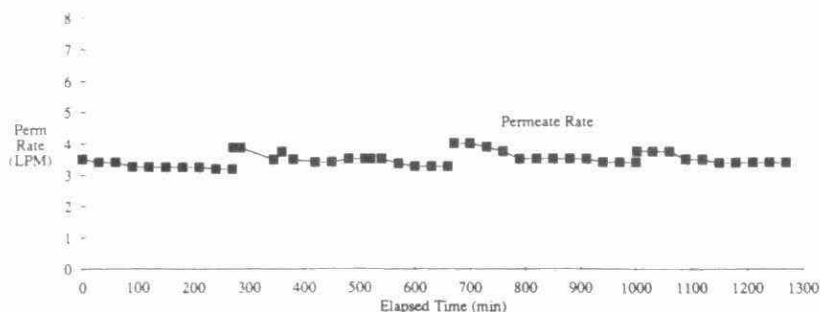


Figure 4
Reverse Osmosis System Operation - Pilot Test #12

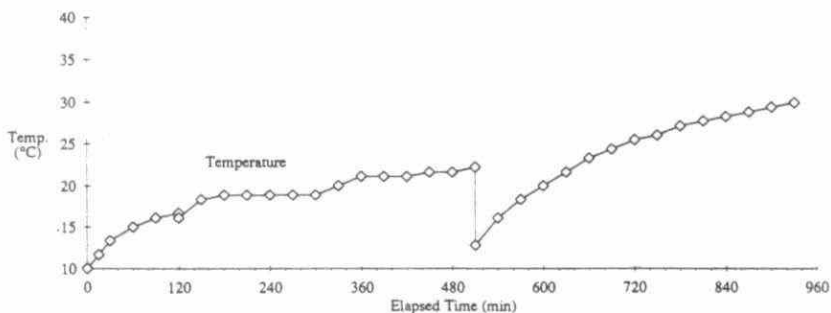
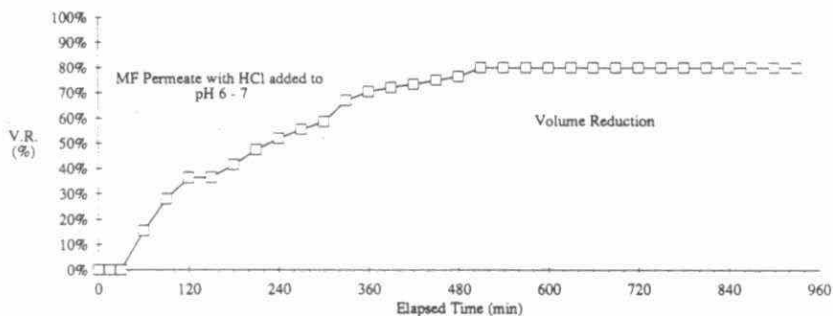
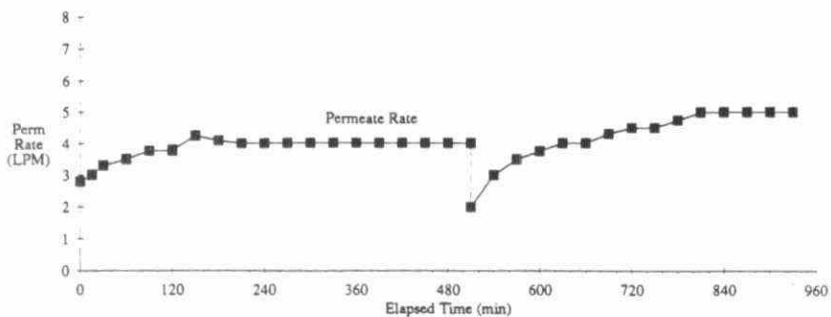


Table 1 - Process Rejections for Test #12

Component	MDL	Raw Leachate	Lime Treated Feed	MF Permeate	% MF Rejection	RO Permeate	% RO Rejection	Total Process Rejection
pH (@ 20 °C)		5.96	8.82	7.42	-	5.79	-	-
Alkalinity (mg/L)		180	950	430	54.7%	20	95.3%	97.9%
TOC (mg/L)	1	158	170	200	-	11	94.5%	93.5%
COD	10	430	470	440	6.4%	43	90.2%	90.9%
BOD5		230	-	245	0.0%	14	94.3%	-
TDS	10	530	630	600	4.8%	130	78.3%	79.4%
TSS	10	230	1200	<	>99.2%	<	-	>99.2%
Fluoride (mg/L)	0.1	<	<	<	-	<	-	-
Chloride	0.2	21	22	22	0.0%	35	-	-
Nitrate (as N)	0.2	<	<	<	-	<	-	-
Bromide	0.8	<	<	<	-	<	-	-
Phosphate (as P)	0.8	<	<	<	-	<	-	-
Sulphate	1	1.8	2.2	2.3	-	<	>56.5%	-
Calcium (mg/L)	0.023	72	230	69	70.0%	8.9	87.1%	96.1%
Magnesium	0.05	10	100	72	28.0%	5.7	92.1%	94.3%
Sodium	0.1	14	14	15	-	2.2	85.3%	84.3%
Potassium	0.5	22	22	23	-	3.7	83.9%	83.2%
Aluminum	0.03	0.078	0.17	0.05	70.6%	<	>40.0%	>82.4%
Barium	0.001	0.24	0.25	0.055	78.0%	0.008	85.5%	96.8%
Beryllium	0.001	0.001	<	<	-	<	-	-
Boron	0.01	0.23	0.22	0.2	9.1%	0.07	65.0%	68.2%
Cadmium	0.002	<	<	<	-	<	-	-
Chromium	0.004	0.005	0.011	<	>63.6%	<	-	>63.6%
Cobalt	0.01	0.02	0.02	<	>50.0%	<	-	>50.0%
Copper	0.006	<	<	<	-	<	-	-
Iron	0.01	130	170	3	98.2%	0.02	99.3%	>99.9%
Lead	0.02	<	<	<	-	<	-	-
Manganese	0.005	2.3	2.6	0.19	92.7%	0.03	84.2%	98.8%
Molybdenum	0.02	<	<	<	-	<	-	-
Nickel	0.01	<	<	<	-	<	-	-
Phosphorus	0.06	<	0.07	0.06	14.3%	<	>0.0%	>14.3%
Silicon	0.05	8.3	9.7	3.5	63.9%	0.35	90.0%	96.4%
Silver	0.01	<	<	<	-	<	-	-
Strontium	0.001	0.45	0.49	0.25	49.0%	0.027	89.2%	94.5%
Sulphur	0.06	1.5	3.3	2.2	33.3%	0.38	82.7%	88.5%
Thallium	0.06	<	<	<	-	<	-	-
Titanium	0.01	0.016	0.023	<	>56.5%	<	-	>56.5%
Vanadium	0.005	0.005	0.008	<	>37.5%	<	-	>37.5%
Zinc	0.005	0.009	0.038	0.018	52.6%	<	-	>86.8%
Zirconium	0.01	<	<	<	-	<	-	-
EPA624 (µg/L)								
trans-1,2 Dichloroethane	1.1	3.8	-	2	47.4%	1.4	30.0%	63.2%
1,1-Dichloroethane	0.5	4.8	-	2.2	54.2%	0.5	77.3%	89.6%
1,2-Dichloroethane	0.4	1.7	-	1.3	23.5%	0.9	30.8%	47.1%
Benzene	0.2	6.9	-	2.9	58.0%	0.8	72.4%	88.4%
Trichloroethane	0.3	2.4	-	1.1	54.2%	1.5	-	37.5%
Toluene	0.3	120	-	72	40.0%	14	80.6%	88.3%
Tetrachloroethene	0.2	1.1	-	0.8	27.3%	0.49	38.8%	55.5%
Ethylbenzene	0.3	22	-	11	50.0%	2.8	74.5%	87.3%
EPA-625 (µg/L)								
Phenol	1.1	300	-	66	78.0%	91	-	69.7%
Naphthalene	0.3	<	-	99	-	24	75.8%	-
Acenaphthene	0.7	32	-	88	-	24	72.7%	25.0%
Fluorene	0.3	24	-	46	-	6.1	86.7%	74.6%
Phenanthrene	0.3	14	-	24	-	7.8	67.5%	44.3%

MDL - minimum detection limit

< - less than MDL

SLOW RATE INFILTRATION LAND TREATMENT AND RECIRCULATION
OF MSW LANDFILL LEACHATE IN ONTARIO

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1. INTRODUCTION

This paper outlines the major results from a 3-year research program (1987-90) conducted by the University of Guelph for the Research and Technology Branch of the Ontario Ministry of the Environment (M.O.E. Project 333G). An interdisciplinary approach was used in this research program in applying established and proven principles and technologies from the natural sciences, particularly agronomy and silviculture ("agroforestry"), in the study of the treatment and disposal of municipal solid waste (MSW) landfill leachates on decommissioned refuse cells or adjacent land areas in Ontario (McBride, 1990).

Slow rate infiltration land treatment systems are designed to circulate wastewater back into the terrestrial (soil-vegetation) ecosystem in such a way that the maximum degree of renovation and attenuation of contaminants is achieved before the effluent re-enters the hydrologic cycle as deep drainage and phreatic water. The ecosystem thus acts as a "living filter" in effecting both physico-chemical and biological decontamination, with soil water recharge and plant nutrient supply being potential ancillary benefits.

The research program had three objectives:

- i) to evaluate slow rate infiltration land treatment of leachate in forested or agricultural ecosystems using alternative land application techniques as a practicable economic, environmentally-sound and long-term solution to landfill seepage occurrences under Ontario biophysical and climatic conditions.

- ii) to evaluate the recirculation of leachate to the landfill surface as a partial on-site treatment method under Ontario climatic conditions.
- iii) to place the technical findings of this study within the context of land use planning for wastewater treatment and disposal.

2. RESULTS AND DISCUSSION

2.1 Characterization of Soil Microbial Responses to MSW Landfill Leachate Irrigation

A soil microbial response study was undertaken to assist in evaluating slow rate infiltration land treatment as an environmentally-sound method of treating MSW landfill leachate. Since it is generally understood that microbial organisms are central to nutrient cycling processes in the soil, emphasis was placed on both the activity and population dynamics of indigenous soil bacteria in both natural forest and agroforestry grassland ecosystems. It was presumed that if leachate had a detrimental effect on soil microbial populations, a reduction in the efficiency of energy transfer and nutrient cycling would occur. A reduction in the efficiency of the biological treatment of the wastewater over the longer term would also be likely.

The activity of the indigenous soil microbial populations was studied in situ using the alkali absorption technique. Soil respiration has been highly correlated with the general decomposer microbial population and has been shown to be relatively sensitive to different forms of toxic contamination. Soil microbial biomass was measured by the direct extraction method. This method has been used extensively to reveal alterations in microbially-active soil environments brought about by a wide variety of stresses, both natural and anthropogenic. An indication of the levels and

nature of the microbial populations present within the soils was obtained using the dilution plate-count method and a morphological system of classification. This method has been widely used to elucidate the effect of various pollutants on soil bacterial populations.

This study revealed that the application of MSW landfill leachate to both forest and grassland ecosystems resulted in an increase in soil respiration. Furthermore, the magnitude of the increase in CO₂ evolution was directly related to the rate of MSW landfill leachate application. Other research has shown a high correlation between the levels of available soil organic matter and microbial activity. It is reasonable to conclude that the increase in observed soil respiration was a function of the application of an irrigant containing ample readily available substrates to the soil. The mode of irrigant application also had a significant effect on the soil respiration rates measured, with sub-surface irrigation generally yielding the highest respiration rates.

As apparent with soil respiration, the application of MSW landfill leachate to the soil resulted in an increased number of soil bacterial isolates. This is most likely due to the introduction of easily decomposed organic substrate materials in the leachate. It is also likely that the application to the soil of a supplemental microbial population present in the leachate itself may cause an increase in microbial numbers over and above indigenous soil populations. Few significant trends were evident, however, when comparing the distributions of morphological classification groups within areas which were previously sprayed with either leachate or water or in areas which served as rain-fed, environmental controls.

Conversely, soil microbial biomass tended to decrease with the application of MSW landfill leachate to both forested and grassed soil

areas. These trends are similar to those reported in the summary report of M.O.E. Project 244G (McBride et al., 1988), where the effect of leachate spray application to a natural forested ecosystem at Muskoka Lakes was investigated. Other research has shown a similar chronic and inhibitory effect on soil microbial biomass with the application of sewage sludge with a high heavy metal content.

2.2 Characterization of Vegetative Responses to MSW Landfill Leachate Irrigation

A study of the physiological responses of hardwood species to irrigation by municipal solid waste (MSW) landfill leachate was conducted in a series of experiments offering a variety of measurement conditions and leachate types. In a natural forested ecosystem, an examination was made of the foliar gas exchange, water relations and spectral properties of understorey sugar maple (*Acer saccharum* Marsh.) sapling leaves subjected to spray irrigation of the Muskoka Lakes leachate. Photosynthetic rates in irrigated saplings were reduced 34% to 53%. Water use efficiency of sapling leaves subjected to direct leachate exposure dropped an average of 70% while leaf temperatures increased 20% and transpiration rates remained constant. Spectral patterns of understorey leaves with leachate residue demonstrated increased absorbance in the near infrared waveband and reduced reflection in visible wavebands. The adaxial spectral properties of mid-canopy leaves (above maximum spray height) of mature sugar maple trees had spectra that suggested increased vigour and benefit derived from leachate irrigation.

A greenhouse experiment examined the response of hydroponically grown red maple (*Acer rubrum* L.) saplings to a series of 4 sub-irrigation treatments with untreated Guelph leachate or deionized water.

the two leachates had an osmotic potential of about -1 kJ kg^{-1} (or MPa), an electrical conductivity of 0.8 to 1.0 S m^{-1} , a chemical oxygen demand of 9.9 to 18.7 g kg^{-1} and a pH of 6.5 to 7.0 . Vegetation tested included reed canarygrass (Phalaris arundinacea L.), meadow foxtail (Alopecurus pratensis L.), weeping willow (Salix babylonica L.) and hybrid poplar (Populus sp. nigra X maximowiczii). Leachate recirculation stimulated height growth by 36% to 141% in the four species tested relative to the growth observed in the water-irrigated control plants. Chlorosis of early season foliage and widespread necrosis and leaf desiccation were visible in leachate-irrigated hybrid poplar and weeping willow saplings after a total leachate application over two seasons of 740 mm . Leaf senescence in the hybrid poplar saplings preceded the normal senescence date by 5 - 6 weeks. By the second field season, stomatal conductance was reduced by 73% , photosynthesis rate by 63% and transpiration rate by 68% in leachate-irrigated hybrid poplar sapling leaves relative to the water-irrigated controls. Vegetative stress was most likely a result of osmoregulation disruption arising from a depressed soil solution osmotic potential. In the reed canarygrass swards, total actual evapotranspiration over the second field season was increased by 50% , height growth by 87% , and foliar biomass production by 160% through recirculation with the more concentrated Guelph leachate in comparison to the water-irrigated reed canarygrass. No phytotoxic symptoms or excessive trace metal accumulations were observed in reed canarygrass leaf tissue. Reed canarygrass shows good potential as a cover vegetation species for leachate recirculation sites under northern temperate climatic conditions.

The field saturated hydraulic conductivity of the silty clay surface covers irrigated with landfill leachate, measured to be in the order of 10^{-5} m s^{-1} , showed a significant increase relative to the water-irrigated surface

covers after a cumulative total irrigant application of 2.9 pore volume equivalents. Volumetric shrinkage of the clay-rich soil cover due to increased effective stresses induced with the application of leachates containing organic solvents and salts was thought to be the cause.

As part of the above recirculation experiment, landfill leachates from these two sources were stored in 200-L holding tanks at ambient temperature for a period of several months at a time. Leachate was removed periodically to irrigate the lysimeters and the recycled irrigants were analyzed for volatile compounds. In the first year, the degradation of chlorinated solvents such as trichloroethylene and tetrachloroethane was apparent with the presence of some of their metabolites, such as cis-1,2-dichloroethene and vinyl chloride. In contrast, the levels of aromatic hydrocarbons remained constant throughout the experiment. These findings are consistent with the generally observed behaviour of these wastewater constituents under anaerobic conditions.

These results were verified during the second year of the recirculation study. In addition, the chlorofluorocarbon Freon-113 was added to several of the holding tanks to monitor its possible biodegradation. The degradation products dichlorotrifluoroethane and chlorotrifluoroethene were observed after two weeks of incubation in the holdings tanks. These compounds were first detected in Ontario in groundwater contaminated by a chemical dumpsite and, up until that time, Freon-113 had been considered refractory to biodegradation. Organic contaminants were also found to breakthrough the 50-cm deep clay layer in the lysimeters independently of their solubility and retardation factors. This indicates that preferential flow probably occurred through fissures in the clay.

These findings are of interest for the management of landfill leachates

because an anaerobic incubation period as a pretreatment step would allow for the degradation of most of the chlorinated solvents. This study also demonstrates that surface clay covers, and possibly bottom liners, may not be a completely reliable means for the prevention of groundwater contamination arising from landfilling operations.

2.4 Physical and Chemical Soil-Leachate Interactions

The inorganic chemical composition and trace heavy metal speciation of four Ontario MSW landfill leachates were investigated. Chemical (and toxicological) analyses showed that the Guelph leachate was the most potent or concentrated and the Leamington leachate was the most benign of the four tested. The Cd concentration of all of the leachate samples exceeded the maximum acceptable level for potable water. The equilibrium chemical computer model GEOCHEM was used to calculate the speciation of trace heavy metals in the landfill leachates. Heavy metals existed as free metals or as complexes with carbonates, hydroxides, chlorides or sulphates. Chloride complexes dominated the aqueous chemistry of leachate cadmium. The retention of cadmium by six soils as a function of pH and initial solution Cd concentration was investigated by adsorption experiments using a batch method. The adsorption behaviour of Cd conformed to the commonly reported pH-dependent adsorption edge. The results of the adsorption experiments were modelled using two surface complexation models. The humic acid model assumes that soil organic matter behaves as a diprotic acid, and the constant capacitance model estimates adsorption on variable charge mineral surfaces. For the six soils examined, humic surfaces are the more reactive at lower pH levels and mineral surfaces become dominant at higher pH levels.

A soil slurry consolidation test protocol was developed that can be used as a pre-screening procedure to determine the degree of physico-

chemical compatibility between various combinations of MSW leachates and natural soil materials potentially destined for use as landfill liners or covers. A comparative decline in total porosity was induced in a clay-rich soil material suspended in Guelph leachate, relative to a distilled water soil slurry, where both were subjected to a range of static loads up to 100 kPa. This led to a corresponding increase in soil strength as the total soil porosity declined, most likely due to the processes of osmotic consolidation and/or osmotic-induced consolidation of the phyllosilicate soil fraction. Under lower overburden pressure conditions, such as on a surface clay cover on a landfill, landfill leachates with a very negative solute potential could cause volumetric shrinkage of the soil matrix and allow preferential flow to occur through the soil.

2.5 Site Selection for the Treatment/Disposal of Leachates on Land

The Soil Potential Rating (SPR) system is a soil-based interpretive classification system that has been developed to rate the relative quality of a soil to support a particular use. Its main advantage over traditional land capability/suitability rating systems is that it emphasizes the concept of potentials or opportunities for use, rather than solely site and soil limitations or constraints.

A methodology was developed for applying the SPR system to the problem of rating soils for their ability to support the land treatment of landfill leachate. Each parameter in the SPR equation was redefined to include both economic costs and measures of environmental quality. A pilot-scale field study at the Muskoka Lakes landfill site was designed to generate soil potential indices (SPI) for three treatment options: spray, trickle and sub-surface irrigation. Each SPI was derived from sub-indices that include ratings of soil performance (P), measures that reflect the type of

irrigation system, or "corrective measures" (CM), and consideration of residual effects, or "continuing limitations" (CL), on the environment. The SPR equation incorporates these sub-indices as follows: $SPI = P - (CM + CL)$.

The careful definition of each sub-index can provide valid, detailed and locally appropriate information that planners need to improve land use decision making with respect to waste management problems. This investigation further illustrated how economic costs and less tangible values, such as the quality of "valued ecosystem components", can be combined in the local level land evaluation process. This methodology can provide valuable input to the MSW landfill site selection process in Ontario, as well as recognition of the need for planning contingencies for treatment and disposal of leachate on adjacent land.

3.0 REFERENCES

- McBride, R.A. (ed.) 1990. Slow rate infiltration land treatment and recirculation of MSW landfill leachate in Ontario. Environment Ontario Research Report. M.O.E. Project 333G. 353 p.
- McBride, R.A., A.M. Gordon and P.H. Groenevelt. 1988. Treatment of landfill leachate by spray irrigation - Muskoka Lakes. Environment Ontario Research Report. M.O.E. Project 244G. 162 p.

Determination of Hydrogeological and Contamination Transport Properties of Fractured, Weathered Leda Clay in Eastern Ontario. A.Y. D'Astous¹ and N.G. Castonguay², 1: Envir-Eau Inc., Hull, Quebec. J8Y 3Y7. 2: Fondex Ltd., Nepean, Ontario. K2E 7V7.

Much of Eastern Ontario is underlain by the Leda Clay, a relatively soft, "impervious" clay of variable thickness. The uppermost part of the clayey deposit is weathered and fractured, up to a few meters, through which pathways exist for contaminant migration. At present, little published information is available on the degree of hydrologic activity in the fractured Leda Clay zone. Burial of municipal or industrial waste in clayey deposits is presently viewed as a safe alternative in preventing extensive migration of contaminants. However, the presence of an active hydrogeological fracture network could provide a lateral and vertical pathway for migration. Due to the recent concern of DNAPL contamination, it is even more necessary to characterize the vertical extent of the fracture network in the Leda Clay. It is therefore our objective to define the depth of fractures and quantify the fracture flow in areas having different thicknesses and depositional environments within the Leda Clay. We will also assess newly developed techniques for determining the depth of the hydraulically active fractured clay. The principal field investigations and the analysis of field data will be conducted during the summer and fall of 1990. We expect that by the beginning of 1991, sufficient data should have been acquired to define the depth of active groundwater zone and to determine whether the new monitoring techniques are appropriate for the Leda Clay.

THE CHARACTERIZATION OF TWO DISCRETE HORIZONTAL FRACTURES IN SHALE

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INTRODUCTION

The quality of water supplies in Southern Ontario is threatened by contaminants, originating from landfills and industrial sites, migrating through fractures within shale bedrock. Discrete fractures which are continuous over large areas often control the fate of contaminants in the bedrock. Flow and mass transport through fractures is generally characterized using a conceptual model whereby the fracture walls are approximated by two smooth parallel plates separated by a uniform opening (aperture). Previous studies have shown that even in relatively small areas this simple conceptual model may not be appropriate and may lead to large errors in the estimation of groundwater velocity (Raven and Gale (1985); Tsang and Tsang (1987); Brown (1987); Novakowski (1988)).

Factors which may lead to deviations from the parallel plate model include fracture surface roughness, tortuosity of the flow paths and fracture contact area. The fracture contact area and the tortuosity of the flow paths is dependent on both the stress and displacement of the two fracture walls. The roughness of a fracture surface is due to the nature of the cracking process or the presence of fracture infilling materials or combination thereof. The variation of hydraulic aperture or hydraulic conductivity in fractured rock can be studied at a number of different scales ranging from the microscopic scale (eg. Brown, 1987) to a rock mass scale in the order of hundreds of metres (eg. Raven, 1986). A considerable amount of research has been undertaken in studying the nature of small-scale fracture roughness (Brown *et al.* (1986); Brown (1987)). Differences between hydraulic apertures and apertures calculated from surface profiles have been attributed to fracture closure (Brown, 1987). Contact area may take the form of abraded areas or single points of contact or a combination of both depending on the mode of fracture formation. Laboratory and modelling studies of natural rock surfaces (Brown and Scholz, 1985; Raven and Gale, 1985; Pyrak-Nolte *et al.*, 1987; Tsang and Tsang, 1987) have shown that as the contact area increases, the parallel plate model provides a poorer description of fracture flux. When

the contact area is greater than 30% of the total area, the flow rate can be depressed by two or more orders of magnitude than would be predicted by the cubic law (Tsang, 1984). The more small apertures there are in the distribution the larger the effect of tortuosity and thus the more error in the estimation using the cubic law (Tsang, 1984).

The description of the spatial variability of geological parameters, such as hydraulic aperture, can be accomplished using geostatistics. Many geological properties such as transmissivity, or fracture aperture fit normal, lognormal or exponential distributions on a spatial or time dependent scale. However, some researchers have found aperture distributions to be skewed. Tsang and Tsang (1987) fit a gamma function to an experimentally derived aperture distribution in a single fracture. Raven (1986) determined a skewed log-normal distribution for a fractured rock mass over a scale of the order of hundreds of metres.

An initial step in the analysis of distributions in order to estimate the parameter at points or areas where no data exists, is the construction of semivariograms (commonly called variograms). Variograms describe the variance of the increment between points in space and depend only on the distance between pairs of sample points. The construction of the variogram assumes that the parameter studied is a random function interpreted as a stationary regionalized variable. An assumption of stationarity implies that the property of the medium is stationary in space and has a constant mean (does not vary with a translation). Weak stationarity refers to a medium where only the mean and variance are stationary at any point in the medium (de Marsily, 1986). These assumptions lead to the 'intrinsic hypothesis' needed for the construction of variograms. The scale at which the data points are correlated can be inferred by fitting an experimental variogram to a theoretical model. Correlation length can be looked upon as being the spatial range within which apertures have similar values. 'Kriging' is a method of interpolating between known data points using a linear unbiased estimator. A thorough discussion of geostatistical methods including kriging is beyond the scope of this report but can be found discussed in detail by Delhomme (1978), Delhomme (1979) and de Marsily (1986).

The purpose of this study is to characterize in detail two discrete fracture zones continuous in an area of about 400 square metres. At this scale the variation of aperture in single fractures can be examined by determinations of hydraulic apertures using in-situ single well tests in different boreholes several metres to tens of metres apart. The aperture distributions determined in this study provide field data at a scale important in investigating flow and mass transport in fractured sedimentary rock. Constant-head injection tests were conducted in 25 boreholes intersecting both fracture planes in order to obtain measurements of the hydraulic aperture. Variograms are constructed for each fracture showing the level of correlation between aperture determinations in different

boreholes. Previous work at this site is summarized in Novakowski (1988).

FIELD STUDY

The study site is located in the town of Clarkson, 50 km west of Toronto, Ontario and approximately 1.5 km north of Lake Ontario. The site is underlain by about 3 m of overburden which is in turn underlain by the Upper Ordovician Meaford-Dundas shale. The shale is highly weathered and fissile near the bedrock surface. Most of the fractures evident in core are bedding plane partings associated with soft mud seams or interbeds of siltstone and fossiliferous dolostone of up to 0.20 m in thickness. The fractures are flat-lying and probably formed as sheeting structure along the bedding planes. During the last four years, a total of 25 boreholes, each 0.038 m in diameter, arranged in a 20 m x 20 m grid (five lines with five boreholes in each line) have been completed at the site (Figure 1). Previous work at the site (Blackport *et al.*, 1986; Mase *et al.*, 1987 and Novakowski, 1988) has led to the identification of two fracture zones which are the focus of current studies. The two fractures or fracture zones are referred to in this report as the upper and lower fracture respectively.

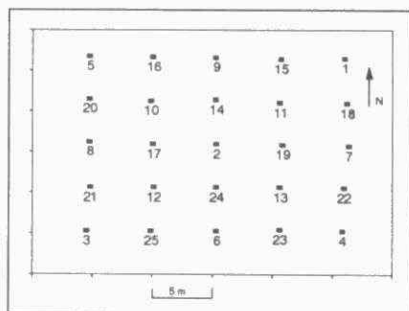


Figure 1: Site map showing all boreholes (boreholes are numbered in the order of completion).

The upper fracture is located approximately 9.8 m below ground surface while the lower fracture is approximately 10.5 m below ground surface. The lower fracture is associated with a fossiliferous dolostone bed which varies in thickness between 0.10 m and 0.18 m across the site. The upper fracture is also associated with a dolostone bed which was identified in 11 boreholes and is less than 0.05 m in thickness.

In order to obtain hydraulic aperture measurements for each of the two fractures in each of the 25 boreholes, constant-head injection tests using packer spacings of variable length were carried out. A

constant-head injection test is conducted by injecting water into a portion of the borehole sealed off between two inflatable packers and measuring the resulting change in pressure at a constant flowrate. Since the vertical distance between the two fractures is approximately 0.70 m, packer spacings less than this distance were employed to ensure that the two fractures were measured separately. A more detailed explanation of the general field methodology employed for constant-head injection tests can be found in Zeigler (1976); Doe *et al.* (1980) and Doe and Remer (1987). A description of the specific testing methodology employed for this study can be found in Novakowski (1988).

METHODS OF ANALYSIS

Fracture aperture can be determined from constant-head injection tests by using a modified version of the Theim equation for steady state radial flow and the cubic law (Witherspoon *et al.*, 1980). Fracture aperture is calculated using the following:

$$2b = \left(\frac{Q}{\Delta H} \cdot \frac{6\mu}{\pi g} \right)^{\frac{1}{3}} \cdot 1 \times 10^{-6} \quad (1)$$

where $2b$ is aperture (μm), Q is the steady state flowrate (m^3/s), ΔH is the difference in hydraulic head between static initial conditions and a steady flow condition (m), r_e is the radius of influence (m), r_w is the radius of the well (m), ρ is the fluid density (kg/m^3), g is gravitational acceleration (m/s^2) and μ is the kinematic viscosity (m^2/s). It is assumed that the results of the constant-head tests represent an average value of the aperture immediately adjacent to the borehole (Novakowski, 1988).

To analyze the statistical nature of the aperture distribution in each of the two fractures, variograms were constructed using the results of the constant-head tests. The experimental variogram can be estimated for values of h which are multiples of a unit distance (lag) by using (Delhomme, 1978):

$$v(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (z(x_i+h) - z(x_i))^2 \quad (2)$$

where $v(h)$ is the variogram, $z(x_i)$ are the experimental values at points x_i such that data are available both at x_i and x_i+h and $N(h)$ is the number of pairs of data points separated by a distance h . Since there was insufficient data suggesting otherwise, the data was assumed to be isotropic. Thus, it was assumed that there was no directional variation in the aperture distributions and that the variations were a function of distance only. This assumption allows the lag distance to be treated as a scalar and the distribution as

one dimensional. Pairs were examined using lag distances which are multiples of the shortest distance between two boreholes. The natural logarithm of aperture ($\ln(2b)$) was used. A total of 160 pairs for each fracture are possible by using the four directions, N-S, E-W, N45E and N45W across the borehole grid. Four lag distances are possible in the N-S and E-W directions and another four in the N45E and N45W directions to obtain a total of 8 lag points from the 160 pairs. Lag distances range from 5.3 m to 30 m.

Three theoretical models are commonly used to fit to experimental variograms. These include a spherical model, an exponential model and a linear model (Delhomme, 1978). By fitting the experimental variogram to a theoretical model, correlation parameters can be determined which can be used for further interpretation and modelling such as kriging.

RESULTS AND DISCUSSION

Over 250 constant-head injection tests were completed this spring in order to determine the location and aperture of both fractures in all of the boreholes. A summary of fracture aperture widths is shown in Table 1. The distribution of apertures in the lower

Table 1. Summary of fracture aperture widths (in micrometers) as determined from the results of constant-head injection tests.

Borehole #	Upper Fracture 2b(μm)	Lower Fracture 2b(μm)	Borehole #	Upper Fracture 2b(μm)	Lower Fracture 2b(μm)
1	90	221	14	106	241
2	66	235	15	94	26
3	138	27	16	<10	<10
4	67	220	17	104	<10
5	<10*	226	18	18	<10
6	80	85	19	<10	248
7	115	98	20	39	243
8	62	15	21	<10	18
9	<10	167	22	58	282
10	<10	<10	23	120	57
11	107	126	24	54	154
12	<10	94	25	120	214
13	<10	<10			

*aperture is below measurement limit of testing system

fracture ranges from 282 micrometers to below detection limit. In the upper fracture apertures range from 138 micrometers to below detection limit. The detection limit for this particular testing system is estimated to be approximately 10 micrometers. The large number of non-detectable apertures results in multi-modal

distributions (Figures 2 and 3) and thus the apertures are not normally or log-normally distributed as is commonly postulated at this scale (eg. Gale et al., 1985).

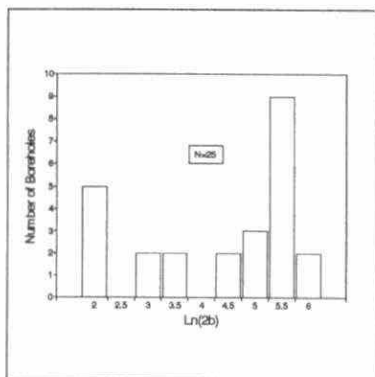


Figure 2: Distribution of apertures for lower fracture.

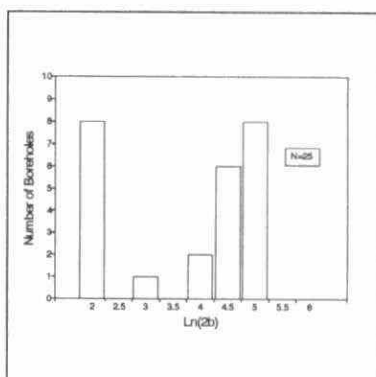


Figure 3: Distribution of apertures for upper fracture.

In 25% of the boreholes the aperture of the lower fracture was below the detection limit and in 32% of the boreholes the aperture of the upper fracture was below the detection limit. This result is interesting and suggests that a scale effect may influence the measurement of the aperture distribution. The reason for the large number of small to non-existent apertures is probably a result of the nature of the proppage of the fracture. For example, this particular area of Southern Ontario, is neo-tectonically active with high compressive-stress oriented horizontally (Lo, 1978). Dynamical stress changes can cause repeated shearing of a small scale in the plane of the fracture. Thus, over time, the asperities or points of contact along the fracture become abraded and flattened. Consequently, the area of contact is increased resulting in a bias towards smaller apertures.

The variograms for both fractures are shown in Figures 4 and 5. For the purpose of variogram construction apertures below detection limit were given a value equal to the detection limit (10 μ m). In constructing the variograms for the upper and lower fractures all data pairs were used. This means that a different number of pairs were summed for each lag distance on the variogram. For example, at a lag distance of 5.3 m (distance between two adjacent boreholes in a N-S or E-W direction) 40 pairs are possible. However, at a distance of 21.2 m (4 x lag distance) only 10 pairs are possible. No attempt was made to adjust the number of pairs

used at each given distance and therefore some bias may be introduced in the analysis. In addition, and perhaps of more severe consequence, the multimodal distribution of apertures may influence the nature of the variogram. Because there is no identified similar examples in the literature, it is assumed that for the following discussion, the variograms are constructed using a log-normally distributed aperture.

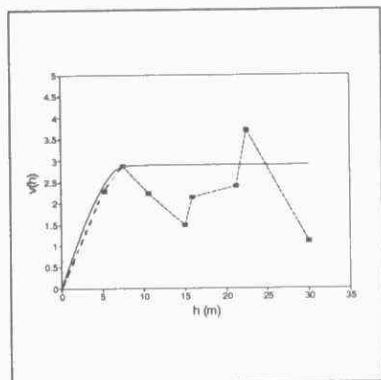


Figure 4: Variogram using aperture distribution of lower fracture.

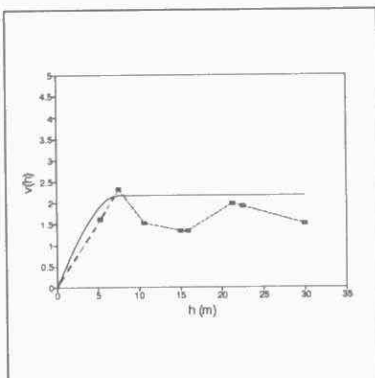


Figure 5: Variogram using aperture distribution of upper fracture.

A spherical model was chosen to fit against the experimental variograms for both fractures. The equation for the spherical model fit is as follows (Delhomme, 1978):

$$\gamma(h) = \omega \left(\frac{3}{2} \frac{|h|}{a} - \frac{1}{2} \left(\frac{|h|}{a} \right)^3 \right) \quad h \leq a$$

$$= \omega \quad h > a \quad (3)$$

This model was chosen assuming that the experimental variograms went through the origin and attained a sill around 10 m. The distance at which the variogram attains the asymptote (or sill) is referred to as the range and shows the extent of the zone of influence of an experimental point (Delhomme, 1978). Using the model fits in Figures 4 and 5 a range of 8 m was determined for the lower fracture and a range of 7.5 m for the upper fracture respectively. This suggests that only the boreholes immediately surrounding a given borehole are spatially correlated. Furthermore, because of the approximate nature of the model fits, correlation lengths much smaller are equally possible. Further

work is necessary in order to investigate both the sensitivity of various model fits and the appropriateness of the chosen model, in addition to the aforementioned problem of the nature of the distribution.

Because determination of a correlation length from the aperture statistics is inconclusive, fracture closure was examined in terms of radius of influence of the hydraulic tests. It was assumed that the radius of influence of a particular hydraulic test could range radially from 0.038 m (one wellbore radius) to a maximum of 2.65 m (half of the distance to the nearest neighbouring borehole). A total fracture area was calculated as 25 m x 25 m square (the area of the grid extended the half distance between boreholes in all directions). The percentage of each fracture plane which is closed can then be calculated assuming that each non-detectable aperture has an equal effect on the total fracture plane. Total fracture contact area is calculated based on a sum of all non-detectable aperture areas.

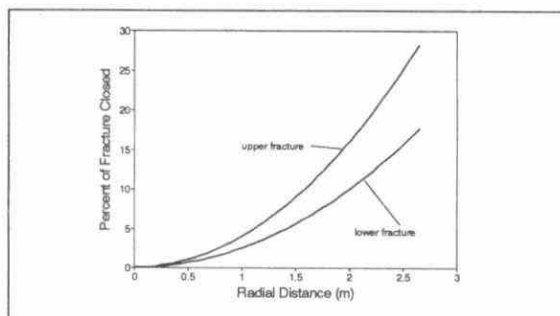


Figure 6: Diagram showing the percent contact area with varying radius of influence of the hydraulic tests.

The purpose of this calculation is to examine the difference in possible contact area based on the radius of influence of the hydraulic tests. In the upper fracture plane a maximum of 28% of the fracture plane may be closed while in the lower fracture a maximum of 18% of the fracture plane may be closed (Figure 6). As both fractures occur at shallow depths (less than 15 m) it seems unlikely that lithostatic pressure (<1 MPa) alone would lead to such large areas of fracture closure. Large areas of closure suggest tortuous flow paths may affect the average velocity of groundwater and contaminants through the fractures and lead to a highly dispersive system. The two curves show that there may be significant differences between the two fracture zones.

SUMMARY

The uncertainty and ambiguous nature of the descriptions of the aperture distributions and variograms in this study indicate that the processes and conditions which lead to fracture formation need to be examined and taken into account in any model of the fracture flow field. The large number of non-detectable apertures found in both fractures suggests potentially large areas of closure. The nature of these areas of closure will have significant effect on mass transport and velocity determinations in single fractures. Previous tracer tests at the site (Novakowski, 1988) found large measurements of dispersion which may possibly be attributed to tortuous flow paths around areas of closure. Kriging the fracture zone planes will yield various simulations of the aperture distributions of the fractures over the study site. Further work is needed to examine the aperture distributions in a stochastic framework in order that realistic models for groundwater velocity and contaminant transport within both of the fracture zones studied can be determined.

REFERENCES

- Brown, S.R. and C.H. Scholz, Closure of random elastic surfaces in contact, *Journal of Geophysical Research*, Vol. 90, No. B7, pp. 5531-5545, 1985.
- Brown, S.R., R.L. Kranz and B.P. Bonner, Correlation between the surfaces of natural rock joints, *Geophysical Research Letters*, Vol. 13, No. 13, pp. 1430-1433, 1986.
- Brown, S.R., Fluid flow through rock joints: the effect of surface roughness, *Journal of Geophysical Research*, Vol. 92, No. B2, pp. 1337-1347, 1987.
- Delhomme, J.P., Kriging in the hydrosiences, *Advances in Water Resources*, Vol. 1, No. 5, pp. 251-266, 1978.
- Delhomme, J.P., Spatial variability and uncertainty in groundwater flow parameters: a geostatistical approach, *Water Resources Research*, Vol. 15, No. 2, pp. 269-280, 1979.
- de Marsily, G., *Quantitative hydrogeology*, 440 pp., Academic Press, London, 1986.
- Doe, T., J. Osnes, M. Kenrick, J. Geier and S. Warner, Design of well testing programs for waste disposal in crystalline rock. In *Proceedings of 6th Congress of the International Society for Rock Mechanics*, Montreal, Canada, 1987.
- Doe, T. and J. Remer, Analysis of constant-head well tests in nonporous fractured rock, In: *Third Invitational well-testing symposium-"well testing in Low Permeability Environments"*, Berkeley California, pp. 84-89, 1980.

- Gale, J.E., A. Rouleau and L.C. Atkinson, Hydraulic properties of fractures, In: Hydrogeology of rocks of low permeability, Memoirs, Intern. Assoc. Hydrogeologists, Vol. XVII, Parts 1 and 2, Tuscon, Arizona, pp. 1-16, 1985.
- Mase, C.W., Thompson, G., Cherry, J.A., Blackport, R., and Smith, L., Evaluation of contaminant velocity in low-permeability fractured shale. In: Proc. Technology Transfer Conference, Ontario Ministry of Environment, Dec., Toronto, Ontario, Canada, 1987.
- Novakowski, K.S., Comparison of fracture aperture widths determined from hydraulic measurements and tracer experiments, In: Proc. 4th. Canadian/American Conf. Hydrogeol., Banff, Alta., pp. 68-80, 1988.
- Pyrak-Nolte, L.J., L.R. Myer, N.G.W. Cook and P.A. Witherspoon, Hydraulic and mechanical properties of natural fractures in low permeability rock, In: Proceedings of the International Society for Rock Mechanics, 6th International Congress on Rock Mechanics, Montreal, Canada, pp. 225-231, 1987.
- Raven, K.G. and J.E. Gale, Water flow in a natural rock fracture as a function of stress and sample size, Int. J. Rock Mech. Min. Sci. & Geomech. Abstr., Vol. 22, No. 4, pp. 251-261, 1985.
- Raven, K.G., Hydraulic characterization of a small ground-water flow system in fractured monzonitic gneiss, Nat. Hyd. Res. Inst. scientific series No. 149, paper no. 30, 133 p., 1986.
- Tsang, Y.W., The effect of tortuosity of fluid flow through a single fracture, Water Resources Research, Vol. 20, No. 9, pp. 1209-1215, 1984.
- Tsang, Y.W. and C.F. Tsang, Channel model of flow through fractured media, Water Resources Research, Vol. 23, No. 3, pp. 467-479, 1987.
- Witherspoon, P.A., J.S.Y. Wang, K. Iwai and J.E. Gale, Validity of the cubic law for fluid flow in a deformable rock fracture, Water Resources Research, Vol. 16, No. 6, pp. 1016-1024, 1980.
- Zeigler, T.W., Determination of rock mass permeability, Waterways Experiment Station, Technical Report S-76-2, Vicksburg, Mississippi, 1976.

The Origin and Distribution of Methane in the Alliston Aquifer Complex.

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INTRODUCTION

The main components of the carbon cycle in groundwater are dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) and a common trace component seems to be methane. However, this hydrocarbon could become a major carbon pool and a potential (explosive) contaminant where is present in high concentration (Coleman, 1976; Barker, 1979). This seems to be the case for groundwater in some parts of the Alliston Aquifer Complex. Many wells that tapped this aquifer produce high volumes of methane. As a result, most of the municipal wells have aeration treatment systems. However, the origin and distribution of methane in this aquifer is not well established.

The presence of methane in groundwater could be associated to in-situ production by reactions mediated by bacteria (methanogenesis) and/or migration of gases from bedrock reservoirs. The last type is called thermocatalytic and is formed by decomposition of organic matter at relative high temperature. Both types of methane are categorized as biotic gases (participation of organic matter in methane formation).

Two hypotheses have been postulated to explain the occurrences of methane in the Alliston Aquifer. One suggests that the occurrence of methane is controlled by the nature of the underlying Paleozoic bedrock. Where the bedrock is shaley (Collingwood, Blue Mountains Groups), insignificant amounts of gas are found. However, where the bedrock is limestone (Trenton Group), methane is found at high concentration. This implies that the source of methane is leakage or migration from the more permeable limestone bedrock. This hypothesis is supported by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other part of Southern Ontario (Barker and Pollock, 1984).

The second hypothesis, based on carbon isotope analyses of methane from some overburden wells, suggests that methane is

biogenic, produced by bacterial action. This implies that the methane is produced within the aquifer, since the methane found in the Trenton rocks has an isotopic composition typical of thermocatalytic methane. Therefore, a bedrock control of the occurrence of methane appears to be unlikely.

This paper presents a summary of results from a research project funded by the Ministry of the Environment, whose main objectives are, to establish the distribution pattern of methane, to determine the origin of methane and to establish a basis for prediction of methane occurrences in the aquifer.

STUDY SITE

This research has been carried out in the Alliston Aquifer complex. This aquifer is a confined, discontinuous, but extensive network of fine to gravelly sand lenses underlain by bedrock or basal till and overlain by clayey till. It seems the aquifer extends from the vicinity of Aurora to Wasaga beach and includes the area northwest along the Nottawasaga Bay (Figure 1). This aquifer is the major water supply for towns such as Alliston, Cookstown, Newmarket and Bond Head and is an essential water resource for an increasing population.

The study area is mostly underlain by rocks of the Simcoe (middle Ordovician) and Nottawasaga (upper Ordovician) Groups. The areal distribution of the various units that formed these groups is shown in Figure 2. The units relevant to this study are the Trenton and Black River Limestone and the Collingwood and Blue Mountain Shales.

APPROACH AND ACTIVITIES

The research approach includes the use of hydrological, geological and geochemical tools. The rationale for this research approach can be found in Aravena et al, 1988.

The main activities carried out during this research can be summarized as follow: A map of the bedrock lithology was constructed to test the hypothesis that the nature of the bedrock controls the distribution of methane in the aquifer; A map of the groundwater flow regime was updated to evaluate the role of the groundwater as a transport medium for the methane; Groundwater from bedrock and overburden wells was sampled to evaluate the distribution of methane; Analyses of carbon isotopes (^{13}C , ^{14}C) in methane and DOC samples were performed to provide information

about the origin and carbon sources for methane; Stable isotopes (^{18}O , ^2H) analyses in groundwater were performed to evaluate the origin of groundwater in the aquifer.

SUMMARY OF RESULTS

Gas analyses

Chromatographic analyses of gas samples indicate that the main components of these gases extracted from groundwater are methane and nitrogen. The average concentration of these two gases are 80 % and 15 % respectively. However, in some groundwater N_2 gas is the main component. ^{15}N analyses are being carried out in some gas samples to provide information about the origin of the nitrogen. Table 1 presents gas composition data for representative gas samples from overburden and bedrock.

Methane concentration data are plotted in Figure 3 for overburden groundwater and Figure 4 for bedrock groundwater. The non continuous line represents the boundary between the limestone and the shale bedrocks. It appears that the area southeast of Alliston towards Beeton has the high concentration of methane, either in bedrock or overburden wells. A trend toward decreasing methane concentration is observed in the area north and northeast of Alliston. No methane was found in overburden and bedrock wells sampled along the west side of the aquifer.

A comparison of the regional distribution of methane with the areal distribution of the underlying Ordovician bedrock indicates that the nature of the bedrock does not influence the distribution of methane in the aquifer.

Environmental Isotopes analyses

Carbon isotope analyses in methane samples present a $\delta^{13}\text{C}$ range between -69 o/oo to -84 o/oo with most of the samples around -75 o/oo. No significant isotopic differences have been noted in methane from overburden and bedrock wells. These data are similar to that reported from some overburden wells by Barker and Fritz (1981). Figure 5 shows the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ distribution of methane gases of different origin. All methane results from the Alliston groundwaters plot in the field of biogenic methane. Furthermore, $\delta^2\text{H}$ data in methane and associated groundwater indicate that the main reaction pathway for methane formation is CO_2 reduction.

Carbon sources for methane

Since DOC could be a potential carbon source for methane, an extensive evaluation of this carbon pool was carried out in the aquifer. These data show a range of DOC concentration between 1 ppm to values as high as 17 ppm (Table 1). Typical DOC concentration are less than 1 ppm in deep groundwater and less than 5 ppm in unconfined aquifers in the Alliston area (Wassenaar, 1990). These high DOC concentration suggests that the groundwater is moving through aquifer materials that are rich in organic matter. DOC and methane concentration present a direct linear correlation, which suggest that both carbon pools are related to a common carbon source.

^{14}C analyses on DOC (hydrophobic fraction) and methane samples supports this hypothesis (Table 2). Radiocarbon ages for carbon pools are in the same age range. However, in some parts of the aquifer, DOC ages are much younger than methane ages. This suggest that methane is transported by the groundwater from production zones to other part of the aquifer. Radiocarbon ages for methane also eliminated the possibility of a significant Paleozoic bedrock carbon source for the methane.

Reports of the presence of organic matter in water well log records published by the M.O.E. also supports the idea of a carbon source for methanogenesis within the aquifer materials.

Origin of groundwater

The stable isotope data (^{18}O , ^2H) in overburden and bedrock groundwater is plotted in Figure 6. This plot shows an isotopic range between -14.3 o/oo and -10.7 o/oo for ^{18}O and -92 o/oo and -78 o/oo for ^2H . This significant isotopic difference implies that at least two types of groundwater are present in the aquifer. The isotopic composition of modern water in the unconfined shallow aquifer in the Alliston area ranges between -10.8 o/oo and -11.5 o/oo for ^{18}O and -78 o/oo and -81 o/oo for ^2H (Wassenaar, 1990). The presence of isotopically depleted groundwater ($^{18}\text{O} = -14.3$ o/oo) in the aquifer suggest that these waters were recharged during cooler climatic conditions than today.

CONCLUSIONS

The main conclusions of this research can be summarized as follow:

- The nature of the bedrock does not control the distribution of methane in the aquifer.
- Methane is formed by microbial processes (methanogenesis) and is not thermocatalytic, as is the case for many bedrock methane sources in Southern Ontario.
- Organic rich sediments present in some parts of the aquifer are the main carbon sources for methane and dissolved organic carbon.
- The distribution of methane appears to be controlled by migratory transport in groundwater from production zones to diferents parts of the aquifer.
- Old groundwater recharged under different climatic conditions than today is present in some parts of the aquifer.

REFERENCES

- Aravena, R., Barker, J.K., Bliss, M., Wassenaar, L.I., and Gillham, R.W. 1988. The origin and distribution of methane in the Alliston aquifer complex. In Proceedings: Technology Transfer Conference, Environment Ontario, Section C, Liquid and Solid Waste. p. 139-151.
- Coleman, D.D. 1976. Isotopic characterization of Illinois natural gases. Ph.D. thesis, University of Illinois, Urbana-Champaign, 175 p.
- Barker, J.K. 1976. Methane in groundwater- a carbon isotope geochemical study. Ph.D thesis, University of Waterloo, Waterloo, Ontario, 310 p.
- Barker, J.K and Fritz, P. 1981. The occurrence and origin of methane in some groundwater flow systems. Canadian Journal. Earth Sciences, 18, (12), p.1802-1816.
- Barker, J.K and Pollock, S.J. 1984. The geochemistry and origin of natural gases in southern Ontario. Bulletin of Canadian Petroleum Geology, 32, (3), p.313-326
- Wassenaar, L.I. 1990. Geochemistry, isotopic composition, origin and role of dissolved organic carbon fractions in groundwater. Unpublished Ph D. Thesis. University of Waterloo, Waterloo, Ontario, 202 p.

Table 1. Chemical composition of representative gas and DOC in water samples, Alliston Aquifer Complex.

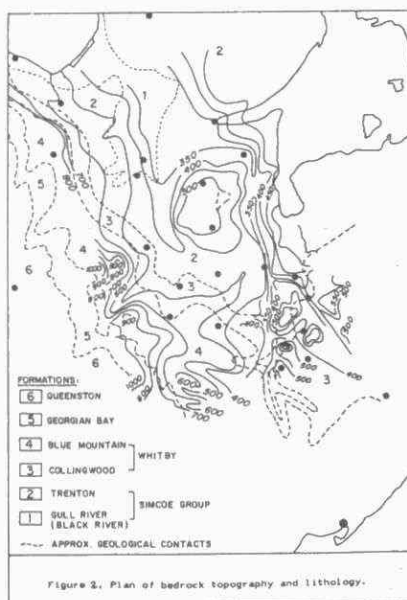
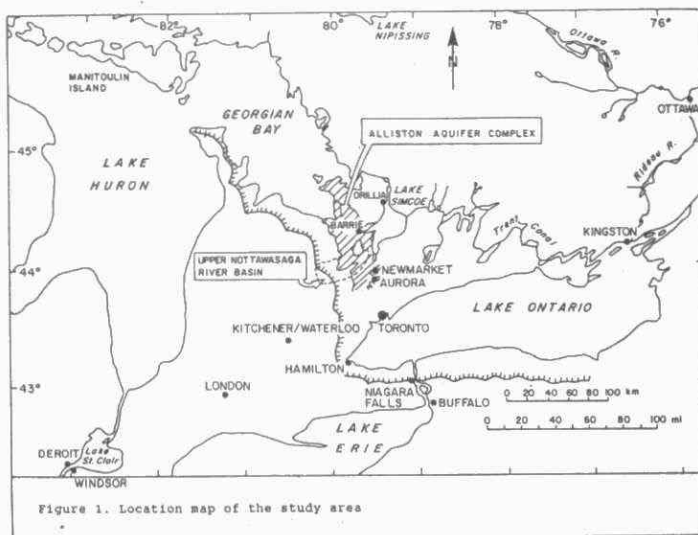
WELL	ELEVATION (ftasl)	CH ₄	N ₂ (%)	O ₂	CO ₂	CH ₄ (uM/l)	DOC (ppm)
BR*	569	87.8	8.25	0.14	0.91	4680	9.3
BR	430	83.2	13.8	0.3	1.15	2180	8.2
BR	470	64.5	35.5	0.80	0.44	2550	5.2
BR	405	7.2	89.3	0.04	0.22	240	0.9
BR	382	31.7	58.7	0.41	0.1	1160	2.0
OV**	574	71.9	27.4	0.50	0.85	2080	7.4
OV	503	79.8	17.8	0.45	1.13	3550	17
OV	494	82.1	13.6	1.2	2.7	2765	8.7
OV	517	44.3	45.8	0.30	0.15	1391	6.8

Table 2. Radiocarbon data of CH₄ and DOC from overburden and bedrock wells

WELL	ELEVATION (ftasl)	MATERIAL	CH ₄ (uM/l)	DOC (ppm)	¹⁴ C AGE (yrs. BP)
OV	466	CH ₄	2750		32,700
		DOC		15	35,500
OV	503	CH ₄	3550		29,600
		DOC		17	26,200
OV	553	CH ₄	2650		40,000
		DOC		9	30,000
OV	511	CH ₄	2780		28,000
		DOC		14	16,800
BR	458	CH ₄	2550		26,000
		DOC		5	9,000

* BEDROCK

** OVERBURDEN



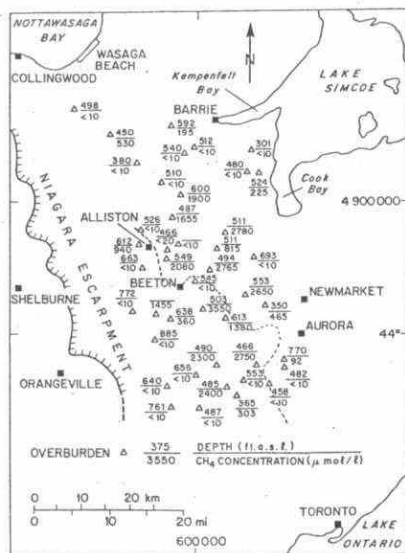


Figure 3. Sampling location and methane concentration in overburden wells, Alliston aquifer complex.

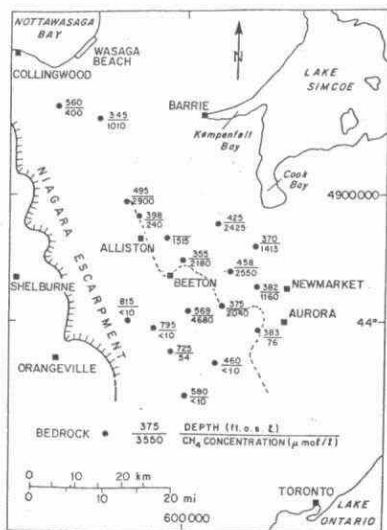


Figure 4. Sampling location and methane concentration in bedrock wells, Alliston aquifer complex.

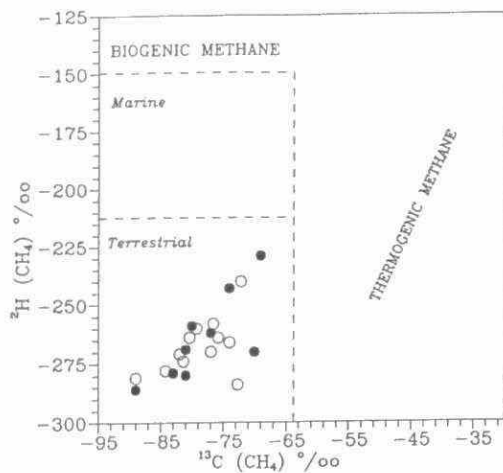


Figure 5. Relationship between the isotopic composition and genesis of methane

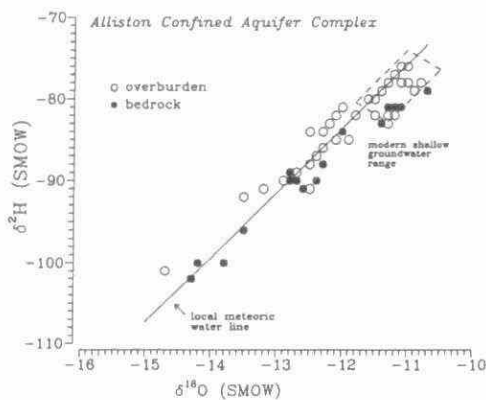


Figure 6. Oxygen-18 and deuterium composition of groundwater, Alliston Aquifer Complex

THE RECYCLING OF STEELMAKING DUSTS USING THE LB FURNACE

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ABSTRACT

Three types of electric arc furnace dusts (with zinc oxide contents at 10, 22 and 37% wt.) and one basic oxygen furnace dust (with zinc oxide content 2.1% wt.) were treated in a bench scale LB furnace⁽¹⁾. Steelmaking dusts were mixed with pulverized coal (various amounts of crushed mill scale were also added to raise the bulk density of the mixture) reduced in the reducing chamber to produce lumpy sponge which dropped by gravity to the melting chamber. In general, 20% wt of coal in the mixture is adequate to complete substantially the reduction. All CO, H₂ and zinc and lead vapours were burned in the combustion chamber to provide the heat requirements to produce sponge at 1000 C. The melting chamber is heated by plasma. Slags and liquid metal made from LB Furnace reduction contain very low amounts of zinc and lead, often at detecting limits of analytical instruments. Zinc and lead oxides in LB Furnace dusts increases with the increase of their contents in the feed materials.

1. INTRODUCTION

Every year, about four million tonnes of lead and five million tonnes of zinc are produced and consumed in the world. In our effort to recycle industrial products (using scrap in steelmaking and in nonferrous foundries) and in the disposal of municipal waste (incineration), heavy metals such as lead, zinc, cadmium, etc., resurface, usually in hazardous dusts. The most feasible solution for the detoxication of these hazardous materials lies in the volatility of heavy metals under a reducing condition in the presence of carbon and/or hydrogen. Zinc, lead, cadmium, etc (originally in either metallic or oxidized state) will become vapours and separate from the materials being treated.

The literature on disposal, recycling and recovery of steelmaking waste oxides are mainly on electric arc furnace (EAF) dusts. A collection of papers in this area⁽²⁾ and a critical review of the problems and potential solutions⁽³⁾ are available. Among various technology proposed two types of approaches may be identified:

- (a) From high zinc EAF dust to metallic zinc

They are usually plasma (or other electrically heated) furnaces with single chamber for reaction. Combustion is avoided to minimize the amount of oxidizing gases such as CO₂ and H₂O which may cause re-oxidation in the condensation metallic vapours.

- (b) From low zinc EAF dust to high zinc dust

Rotary kiln and slag fuming are common approaches. Coal is usually the energy source. It has been often suggested as the choice for regional treatment center to have the economy of size.

In the literature, two concerns have been often expressed. They are energy efficiency and the need of agglomeration of dusts.

2. THE LB FURNACE

The work on LB furnace initiated in the early 1980's at McMaster University is aimed to develop a coal-based ironmaking process using fine ore and pulverized coal⁽¹⁾. In order to have high energy efficiency, coal is first used as reductant then as a fuel. The advantages include large reacting surfaces, no agglomeration nor coking is required and very high energy efficiency.

The LB furnace may be divided into two chambers: (1) the reduction/combustion chamber and (2) the melting chamber, as shown in Fig. 1. The former consists of the reaction tube and the combustion chamber, and the latter a plasma-heated crucible. It may be used to make sponge iron (with plasma off) and to have it melted in other types of vessels.

Mixtures of coal, dust, ground mill scale and fluxes are moved mechanically with the use of a steel screw feeder through a silicon carbide tube to the combustion chamber. The tube is 1200 mm long and 83 mm I.D. Hot gaseous products and sponge iron are discharged at the hot end of the tube in the middle of the combustion chamber. Sponge iron which is protected from re-oxidation by the outgoing hot gas until it drops into the melting chamber. The hot gas consists mainly of CO, H₂, metal vapours and very small amounts of CO₂ and H₂O. When the gas is burned in the combustion to provide heat for reduction, metal vapours are burned to oxides and collected in the baghouse.

3. EXPERIMENTAL PROCEDURES

At the beginning of each experiment, a natural gas burner is used to heat up the structure of reduction/combustion chamber for about 90 to 120 minutes. For the treatment of dust, the feeding of solids starts when the thermocouple near the hot end of the reaction tube reaches 1050 to 1100°C, the steady state temperature is 1200 to 1250°C. The cutting of nature gas to the burner begins at the time charging of solids starts and completely off in about 15 to 30 minutes. The power to plasma furnace starts at about the same time to keep the melting chamber at a temperature of 1550°C. The charge rate is about 10 kg per hour and the linear velocity of solids in reaction tube is 60 mm/min. The residence time of solids inside the combustion chamber is about 4 minutes.

4. MATERIALS

Four types of steelmaking dusts and the slag from secondary lead smelting were used for this investigation. Five concentration levels of zinc oxide in these five kinds of waste oxides, from 0.3 to over 30% wt., have been studied. Mill scale was used for two purposes: (A) there are oily mill scales to be disposed of, and (B) the addition of mill scale improves the density and strength of sponge iron. Compositions of these materials and sand are listed in Table 1. Both coal and mill scale are ground to 95% -300 µm or finer. No attempt was made to dry these materials because they appear to be very dry.

5. EXPERIMENTAL RESULTS

Experimental data of the first series of runs on low zinc EAF dust are listed in Table 2. In Table 2A, the makeup of mixtures of waste oxides, high volatile coal and fluxes are listed. In these mixtures, ranges of zinc oxide and lead oxide contents are 3.8 to 7.5 and 0.8 to 1.6% wt., respectively. The weights of reaction products (dust, slag and liquid metal) are given in Table 2B. Total dust is listed which means the sum of baghouse dust and cyclone dust, the latter contributes less than 5% in weight and slightly lower in zinc and lead contents. Reports on the weights of reaction products in all other experiments will be omitted to avoid repetition. In Table 2C, the compositions of reaction products are presented. The recovery of volatile heavy metals in the dust collected are given in Table 2D.

Results of treating EAF dusts with medium and high zinc contents are listed in Table 3. Zinc oxide and lead oxide in mixture of Exps. 11 and 17 with EAF dust of medium zinc oxide and lead oxide contents are in the range of 8.4 to 16.3 and 1.16 to 2.25% wt., respectively. The corresponding values for Exps. 21 and 22 for high zinc EAF dust are 14.1 and 3.55% wt., respectively.

Five experiments with two levels of BOF dust in the mixture were carried out, see Table 4. In Table 5, results of experiments for treating slag from secondary lead smelting are listed.

6. DISCUSSIONS

The purposes of the treatment of waste oxides with volatile heavy metals in LB Furnace are:

- (1) To enrich zinc and lead oxides in LB Furnace dust so that it could be the feed for economical extraction of zinc, lead and possibly Cd.
- (2) To produce iron alloys and slag to be used in steel plant or to be safely disposed.

The compositions of slag and iron alloys produced in our laboratory are listed in Table 2C, and Tables 3 to 5. They are clearly suitable for re-use or disposal.

Correlation between zinc and lead oxide in the mixture to be fed to LB Furnace and that in the dust collected are shown in Figs. 2 and 3, and the enrichment ratios in Figs. 4 and 5. One may conclude from Fig. 2 that LB Furnace will produce dust of zinc oxide at 30% or higher from all four kinds steel-making dusts studied under a variety of conditions. From Figs. 4 and 5, the effectiveness of LB Furnace in treating low zinc and lead waste oxides are clearly shown. Lines in Figs. 2 to 5 are arbitrarily drawn. It should be pointed out that data points outside of these bands are usually that involving lead slag.

There are at least two mechanisms by which individual particles ended up in the dust collectors in LB Furnace.

- (i) The re-oxidation of gaseous metals
It is almost certain that most zinc vapours, if not all, generated in the reduction tube and the rest in the melting chamber. In the combustion chamber, zinc vapour is burned along with carbon monoxide in the flame. The behaviour of lead would be essentially the same, except that in proportion, there may be slightly more lead gasified in the melting chamber because it has relatively lower equilibrium vapour pressure.
- (ii) The carry-over of solid particles
Lime, iron oxide and other refractory oxides found in baghouse arrived there in fine particles and did not go through the reaction paths of gasification and reoxidation. These fine particles could be available for gas flow to carry it over to baghouse under the following two conditions:
 - Lower degree of reduction which leads to a lower degree of agglomeration of sponge iron at the moment of its discharge to melting chamber, would generate dust from the fine materials in the reaction mixtures.
 - The other possible mechanism is due to carbon boil in slag/metal system. It is unlikely to be important because of a relatively low level of de-carburization rate in this system.

7. CONCLUSIONS

The reduction of steelmaking dusts containing zinc oxide from 2 to 30% wt. by coal has been carried out in LB Furnace which consists of a reduction/combustion chamber and an electrically heated chamber for the melting of slag and metal. The following conclusions may be reached:

- (a) Slags and metal ingots made from LB Furnace reduction contain very low amounts of zinc and lead, often at detecting limits of analytical instruments.
- (b) Zinc and lead oxides in LB Furnace dust increases with the increase of their contents in the feed materials. It has been observed to be in the range from 30 to 60% wt. ZnO and from 8 to 10% wt. PbO for steelmaking dusts.
- (c) The enrichment of ZnO and PbO increases with the decrease of their contents in the feed materials ranging from 45 to 5 times for ZnO and 20 to 4 times for PbO for steelmaking dusts.
- (d) For the reduction of lead slag, the LB Furnace dusts could have PbO concentration as high as 50% wt., and an enrichment ratio of about 8.

8. ACKNOWLEDGEMENT

Financial supports from Ontario Ministry of Environment and Canadian Steel Environment Association are very much appreciated.

9. REFERENCES

- (1) W-K. Lu, C. Bryk and H.Y. Guo, "The LB Furnace for Smelting Reduction of Iron Ores", Proceedings of 5th International Iron and Steel Congress, Vol. 6, pp. 1065-1075 (1986), and U.S. Patent #4,756,748 (1988).
- (2) "Disposal, Recycling and Recovery of Electric Arc Furnace Dust", A collection of papers published by AIME, Iron and Steel Society, AIME (1985).
- (3) "Disposal, Recycling and Recovery of EAF Dust", A report published by Centre of Metals Production, Mellon Institute, 4400 Fifth Avenue, Pittsburgh, PA, U.S.A. (1987).

Table 1: Chemical Analysis of EAF and BOF Dusts, Mill Scale, Lead Slag
and Sand, in Wt.%

Oxides*	EAF 1	EAF 2	EAF 3	BOF	LEAD SLAG	MILL SCALE	SAND
ZnO	10.30	22.68	37.20	2.10	0.32	—	—
PbO	2.16	3.12	9.35	1.10	4.33	—	—
CdO	0.05	0.10	0.08	0.01	0.0002	—	—
SiO ₂	3.50	3.04	2.27	2.10	11.55	0.34	55.3
Al ₂ O ₃	0.64	1.27	0.56	0.10	3.50	0.11	1.90
FeO	45.80	36.77	25.80	63.30	61.20	73.03	1.59
MgO	5.14	2.44	1.93	5.55	1.65	0.003	3.70
CaO	20.98	15.55	14.04	23.60	6.90	0.10	18.00
Na ₂ O	2.50	1.15	2.66	0.20	3.15	0.01	0.70
K ₂ O	2.31	0.70	0.99	0.15	0.20	0.001	1.14
TiO ₂	0.08	0.07	0.05	0.05	0.28	0.005	0.20
MnO	2.33	4.01	3.06	1.49	0.60	0.89	0.03
P ₂ O ₅	0.19	0.11	0.14	0.06	0.68	—	—

* Chemical analysis was carried out by X-ray Fluorescence Method.

Table 2-A: Compositions of Reacting Mixtures, % Wt.

RUN #	1	2	3	4	5	6	7	8	9
EAFF DUST	37.0	37.0	37.4	37.4	20.0	20.0	53.0	53.0	73.0
MILL SCALE	37.0	37.0	37.4	37.4	57.0	57.0	20.0	20.0	-
COAL	18.6	18.6	18.7	18.7	20.0	20.0	20.0	20.0	20.0
GLASS SCRAP	7.4	7.4	3.7	3.7	3.0	-	-	-	-
SAND	-	-	2.8	2.8	3.0	3.0	7.0	7.0	7.0

Table 2-B: Weights of Reaction Products, Kgs

RUN # PRODUCT	1	2	3	4	5	6	7	8	9
SLAG	2.66	2.45	3.38	2.80	1.50	1.90	2.16	2.25	2.10
METAL	7.90	6.90	6.80	7.10	6.20	7.95	3.85	4.30	3.10
TOTAL DUST	1.60	1.40	1.80	1.60	0.87	1.10	1.90	1.80	2.10

Table 2-C: Chemical Compositions of Reaction Products, % Wt.

RUN # PRODUCT	1	2	3	4	5	6	7	8	9
BAGHOUSE DUST									
ZnO	37.3	36.4	35.2	39.6	30.0	31.0	37.8	38.9	44.8
PbO	6.2	7.8	7.4	4.9	5.9	6.6	8.1	8.9	11.8
FeO	29.3	23.1	22.9	23.1	36.6	30.7	26.8	26.8	16.8
CdO	.089	.118	.012	.113	.087	.109	.129	.129	.139
SLAG									
ZnO	.001	.001	.001	.001	.001	.001	.001	.002	.001
PbO	.001	.001	.001	.001	.001	.001	.002	.001	.002
FeO	7.79	4.34	7.65	3.95	3.78	7.45	7.53	5.46	3.70
CdO	.002	.002	.002	.002	.002	.002	.001	.001	.001
METAL									
Zn	.002	.001	.002	.002	.002	.001	.001	.002	.002
Pb	.002	.008	.001	.001	.001	.001	.001	.002	.001
Cd	.002	.002	.001	.002	.002	.002	.001	.001	.002

Table 2-D: Recovery of Zn, Pb and Cd in Dusts Collected at the LB Furnace, %.

RUN # ELEMENT	1	2	3	4	5	6	7	8	9
Zn	72.9	76.9	90.0	70.5	84.4	70.8	85.6	73.8	78.5
Pb	55.8	62.0	50.6	65.3	86.0	95.5	96.5	83.9	94.1
Cd	64.6	36.9	98.5	49.3	52.1	66.7	66.5	52.3	56.7

Table 3: Experimental Results with Medium and High Zinc EAF Dusts.

RUN #	11	12	13	14	15	16	17	21	22
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Composition of Reacting Mixture, % Wt.

DUST	EAF 2							EAF 3	
	37.2	37.2	37.2	37.2	54.0	54.0	72.0	38.0	38.0
Mill Scale	37.2	37.2	37.2	37.2	20.0	20.0	-	38.0	38.0
Coal	18.6	18.6	18.6	18.6	20.0	20.0	20.0	20.0	20.0
Glass Scrap	7.0	7.0	7.0	7.0	6.0	6.0	3.0	-	-
Sand	-	-	-	-	-	-	5.0	4.0	5.0

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST									
ZnO	44.3	39.9	47.3	41.3	54.6	57.8	58.9	59.4	52.9
PbO	10.2	8.0	5.0	6.9	9.1	8.8	11.6	10.1	9.9
FeO	22.6	19.9	20.9	23.1	7.3	5.5	9.9	17.6	9.6
CdO	0.16	0.29	0.13	0.13	0.13	0.12	0.09	0.10	0.10
FeO in Slag	2.9	2.2	2.3	3.5	2.1	2.3	0.87	6.0	4.3

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	60.0	59.4	70.8	57.7	68.9	84.3	67.0	75.9	66.3
Pb	90.2	82.9	59.7	70.4	76.0	88.9	97.4	73.5	49.0
Cd	69.5	98.7	76.2	71.9	39.8	51.1	64.6	90.1	81.0

Table 4: Experimental Results with BOF Dusts.

RUN #	31	32	33	34	35
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Composition of Reacting Mixture, % Wt.

BOF DUST	37.0	35.5	38.0	38.0	80.0
Mill Scale	37.0	36.3	39.0	39.0	-
Coal	19.0	21.4	23.0	23.0	20.0
Sand	7.0	6.8	7.0	7.0	14.0

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST					
ZnO	36.9	30.9	28.7	29.8	34.8
PbO	8.93	8.10	5.95	7.10	9.94
FeO	36.9	33.8	12.7	29.8	30.7
CdO	0.09	0.08	0.08	0.07	0.001
FeO in Slag	6.1	4.8	4.1	4.9	21.1

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	97.1	94.3	97.2	94.7	82.7
Pb	56.0	60.6	45.8	43.9	49.5
Cd	68.0	72.1	64.3	70.2	-

Table 5: Experimental Results with Slag of Secondary Lead Smelting.

RUN #	41	42	43	44
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Composition of Reacting Mixture, % Wt.

Lead Slag	83	83	79	77
Coal	17	17	21	23
Lime	-	-	4.5	4.5

Chemical Composition of Reaction Products, %Wt.

BAGHOUSE DUST				
ZnO	13.2	13.4	5.37	7.17
PbO	26.6	26.2	54.3	30.3
FeO	38.6	30.3	14.0	24.6
CdO	0.02	0.02	0.002	0.001
FeO in Slag	16.4	14.2	2.14	5.54

Recovery of Zn, Pb and Cd in LB Dust, %.

Zn	99.2	95.6	82.0	122
Pb	29.2	26.4	59.5	37.1
Cd	44.0	40.2	-	-

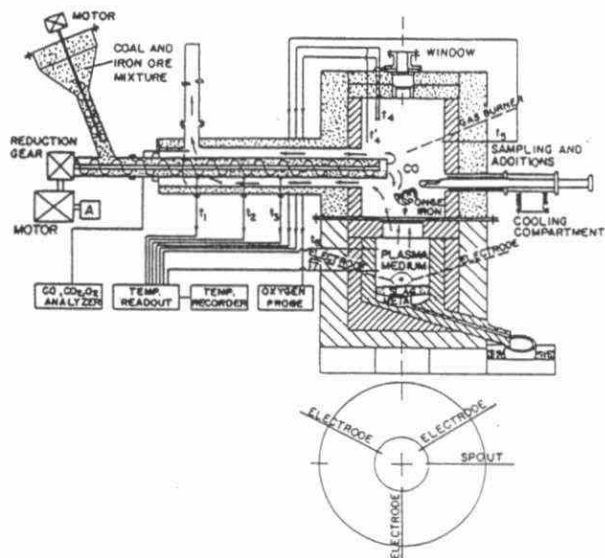


Fig. 1: Cross-Section of the Bench-Scale LB Furnace.

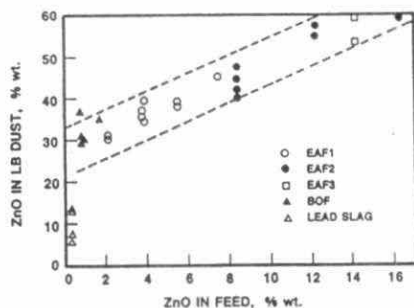


Fig. 2: ZnO in the Feed vs. ZnO in LB Furnace Dust.

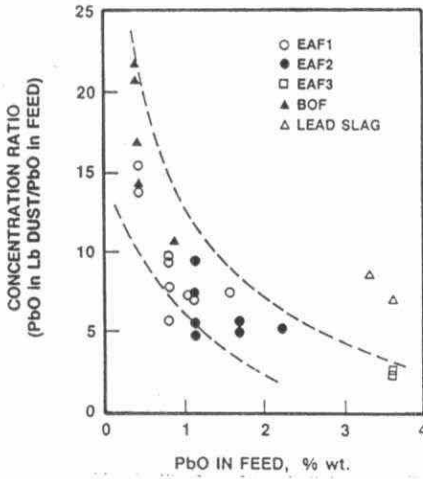


Fig. 5: Enrichment of PbO oxide in LB Furnace Treatment.

In Situ Biodegradation of Chlorinated Solvents. D.W. Major* and E.W. Hodgins, Contaminant Hydrogeology Services, Beak Consultants Limited, Guelph, Ontario, N1H 3Y5

Chlorinated ethenes, such as tetrachloroethene and trichloroethene, are dense, non-aqueous solvents which have solubilities 3 orders of magnitude greater than their respective drinking water limits. Their physical properties and their ubiquity in manufacturing and service shops have led to these compound being one of the most frequently encountered groundwater contaminants. PCE can be sequentially dechlorinated anaerobically to form vinyl chloride (VC), which is an undesirable end-product. A field investigation at a chemical transfer facility indicated that PCE had entered subsurface and had contaminated the groundwater. What was interesting is that the extent of VC distribution was not as great as would be expected if it was persisting in the groundwater. The objective of our research was to gain insight into the possible microbial processes that may be responsible for the degradation of tetrachloroethylene (PCE) and its degradation products, particularly VC. Our initial field study has indicated that methanol (stored at the facility) and acetate were present in the groundwater. Methanol may be promoting the degradation of PCE past VC, whereas, acetate may promote the formation of VC. This conclusion is based upon the ratio of VC/PCE or VC/TCE in monitoring wells as compared to the presence or absence of methanol or acetate. The presence of ethene and ethane in groundwater samples may imply the degradation of VC by undergoing another reductive dehalogenation step forming ethene (which may be further undergo the equivalent of catalytic hydrogenation to form ethane). Gossett and Freedman (1989) have shown in laboratory studies that methanol promotes the degradation of PCE and TCE to ethylene gas under methanogenic conditions. The detection of ethene at our site provides collaborative field evidence of laboratory results indicating that complete dechlorination of PCE and TCE can occur and be environmentally significant. Acetate is an interesting co-contaminant at the site. It is possible that acetogens are forming acetate from the metabolism of methanol. The high concentration of acetate in samples from one groundwater well, which had highest concentration of methanol, supports this possibility. Current work is focusing on characterizing the microbial community using classical microbiological techniques and lipid analysis of authentic core material from the site. Microcosms experiments are evaluating the effect of methanol and acetate on the degradation of PCE. Future work entails the use of *in situ* test columns for controlled field experiments aimed at selectively inducing microbial populations to degrade PCE and VC.

CLASSIFICATION AND LEACHABILITY OF HAZARDOUS WASTES AND HAZARDOUS WASTE RESIDUES. K.B. Harvey, Geochemistry and Applied Chemistry Branch, AECL Research, Whiteshell Laboratories, Pinawa, Manitoba ROE 1LO

In work reported at the 1989 Technology Transfer Conference, it was shown that the non-volatile heavy metals present in waste residues such as sludges and incinerator and furnace ashes could be successfully immobilized in a waste form based on a soda-lime glass. When subjected to the Regulation 309 Leachate Extraction Procedure, the release of heavy metals lay between 3 and 4 orders of magnitude below that from the raw waste. When subjected to serial leaching tests, the releases of heavy metals were below chemical detection limits, but release rates of $\sim 1 \times 10^{-9}$ g/cm²·d were inferred from radioactive tracer experiments.

In a climate of increasing regulatory scrutiny, it will become necessary not only to demonstrate that current releases of heavy metals from disposed waste forms into the environment are acceptably low, but also that there is a sound basis for projecting these release rates into the future. This paper outlines the development of theoretical models that describe release from glassy waste forms, together with preliminary results from experiments designed to verify the models.

NON-LINEAR SORPTION OF PHENOL ON NATURAL CLAY AND ITS INFLUENCE ON DIFFUSIVE MIGRATION

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ABSTRACT

Phenol (C_6H_5OH) sorption onto soil solids is shown by batch testing to be a non-linear function of pore water concentration, with much greater sorption at low concentrations. This results in K_d values ranging from 3 mL/g at low concentrations (~ 0.5 mg/L) down to 0.5 mL/g at high concentrations (~ 100 mg/L). As a consequence of non-linear sorption, the magnitude of the source concentration can affect the rate and distance of solute migration, a feature not observed for constant K_d . Simulated profiles using POLLUTE are presented to demonstrate the significance of the batch test observations.

INTRODUCTION

Disposal of solid wastes to land has been the most prevalent means of disposal in the past and, it appears, will remain so well into the foreseeable future. The growing interest in and practice of recycling and the development of new waste processing techniques may alter the quantity and nature of the waste, but a residue requiring disposal will inevitably remain.

Phenol is a common constituent of municipal landfill leachates typically at concentrations of ~ 5000 $\mu\text{g/L}$ which is several orders of magnitude higher than the Ontario Ministry of the Environment's drinking

water maximum of 2 $\mu\text{g/L}$. It is also widely used in the synthesis of many industrial chemicals and is generated as a waste product from numerous industries and, thus, finds itself in numerous industrial landfill leachates. It is moderately toxic to humans and causes disagreeable odours in drinking water at very low concentrations. The U.S. E.P.A. has classified phenol as a priority pollutant.

The driving processes in the migration of phenol in soil are advection and diffusion, modified by attenuating processes of adsorption, and chemical and biochemical degradation. This paper presents the results of sorption tests conducted with phenol in aqueous solution and examines the potential implications of the observed sorption characteristics.

THEORY AND BACKGROUND

Sorption is a term used to describe the process of solute removal from solutions by soil solids. It includes both adsorption, the transfer of solute to the surface of soil solids, and absorption, the transfer of solute to the matrix of soil solids. For soils containing solids such as organic matter, adsorption would normally be expected to be much more dominant than absorption.

One method for determining the degree to which a solute will sorb to soil solids is batch testing. In batch tests a known mass of soil is shaken as a slurry with a known volume of solution containing a known concentration of the solute of interest. After a period of time (hours to days) the degree of partitioning is determined by measuring the change in solution concentration. Batch test results are "optimum" sorption values since the exposure of the sorbate (the solute) to the sorbent (the soil) is maximized by mixing.

To describe the equilibrium relationship between mass of solute sorbed per unit mass of soil to the concentration of solute remaining in the liquid phase, the equilibrium equation or isotherm commonly used in soil systems is the Freundlich Isotherm. It has the form:

$$[1] \quad x/m = KC^{1/n}$$

where x is the mass of solute sorbed on the soil, m is the mass of soil, K is a constant indicative of sorptive capacity (Zytner et al., 1989), C is the solution concentration after sorption, and $1/n$ is a constant indicative of sorption intensity (Zytner et al., 1989).

The constants shown in [1] are determined by plotting the mass sorbed versus the equilibrium concentration on double logarithmic paper. Typically, a log-linear distribution of the data points results from which K is obtained from the intercept and $1/n$ is obtained from the slope of the curve.

The distribution or partitioning coefficient, K_d , is commonly used to describe the partitioning of the solute between the liquid and solid phases. It is taken from the slope of the isotherm:

$$[2] \quad K_d = \frac{d(x/m)}{dC} = \frac{d(KC^{1/n})}{dC}.$$

If $1/n$ equals 1 then the isotherm will also plot linearly in arithmetic space and the magnitude of K_d will equal K . The linear distribution coefficient has been widely used to describe the sorption of organics on soil (Karickhoff et al., 1979; Banerji et al., 1986; Zytner et al., 1989; Johnson et al., 1989). And although some authors have noted the fact that $1/n$ can be significantly less than 1, apparently there has been little or no study of the consequences of assuming linear sorption.

Johnson et al. (1989) observed "highly non-linear sorption isotherms" for the hydrophobic organic compounds trichloroethene, benzene, toluene, and ethylbenzene in aqueous concentrations between 0.1 and 25 mg/L in Sarnia area clayey soils. However, they chose to represent sorption in terms of a linear K_d , based on batch sorption experimental data conducted at solution concentrations of ~ 1 mg/L. The batch test experimental data were not presented with the paper. Similarly, Banerji et al. (1986) reported non-linear sorption of pentachlorophenol on soils but chose to

present a linear K_d . They state that "most contaminant models treat adsorption as a linear function because of difficulties a non-linear adsorption term creates in solving the governing differential equation".

This paper presents the results of 24-hour batch tests on "unmodified" soil-phenol solution mixtures with the partitioning coefficient, K_d , determined using the Freundlich equation. "Unmodified" means that the physical and chemical characteristics of the soil and slurry were not altered by the addition of chemicals or removal of constituents. Since different soils may have different adsorption equilibrium times due to differing physical properties such as the organic carbon content and surface area (Zytner et al., 1989), kinetics tests were performed to evaluate the validity of the 24-hour testing time.

MATERIALS AND METHODS

A sample of clayey soil from 7 metres depth in a background borehole at the LaSalle Road industrial waste landfill site was air dried, pulverized and well mixed to ensure representative subsampling. The x-ray powder patterns and the traces for oriented fines indicated abundant quartz, carbonate, illite and chlorite, moderate amounts of feldspar and a trace of smectite. The fraction of organic carbon, determined using a modified Walkley-Black technique (Allison, 1965) was 0.78%.

Masses of the air dried soil were mixed with aqueous solutions of phenol in 25 mL Corex glass centrifuge tubes with Teflon-lined seals held in place by plastic screw caps. The mixtures were shaken with a "wrist action" shaker in the absence of light at laboratory temperatures ($\sim 23^\circ\text{C}$). Equilibrium phenol solution concentrations ranged from 100 mg/L to 0.5 mg/L. Ratios of the mass of soil to the mass of aqueous phenol solution ranged from 0.02 to 1.6. These ratios are significantly lower than natural in situ ratios, which are typically 4 to 5. Thus, the degree of sorption was optimized in the batch tests by having large solution volumes.

After 24 hours, the tubes were centrifuged to separate the soil from the solution and the amount of phenol solute remaining in aqueous solution was determined by gas chromatography. The difference between the initial and final equilibrium concentration was designated as being sorbed by the soil.

RESULTS

The sorption of phenol on this soil is described by the Freundlich isotherm with constants, $K = 2.0$ to 3.3 and $1/n = 0.628$ when C is in units of mg/L and x/m is in units of mg phenol per kg dry soil. Because $1/n$ is not close to unity the isotherm should not be taken as linear. Thus, the sorption coefficient, K_d , does not have a unique value for all equilibrium concentrations, C , and is described by:

$$[3] \quad K_d = 1.256 \cdot C^{-0.372} \text{ to } 2.682 \cdot C^{-0.372}.$$

This relationship is shown graphically on Figure 1.

Because phenol dissolves almost exclusively in molecular rather than ionic form, the ion exchange sites of charged clay minerals probably are not significant sorption sites. Various authors (Hamaker and Thompson, 1972; O'Connor and Connolly, 1980; Morrill et al., 1982; Voice et al., 1983; and Zytner et al., 1989) cite soil organic matter as the principal sorption sites for dissolved organic molecules. Phenol is also considered to sorb mainly at organic sites. Many authors normalize the sorption of organics with the fraction of organic carbon as described by Karickhoff et al. (1979). The resultant organic carbon distribution coefficient, K_{oc} , for phenol is:

$$[4] \quad K_{oc} = \frac{K_d}{f_{oc}} = 161 \cdot C^{-0.372} \text{ to } 344 \cdot C^{-0.372}.$$

DISCUSSION

Linear isotherms suggest that the sorption of a solute on a soil increases indefinitely with the concentration of solute, independent of the mass of sorbent. Clearly, an infinite number of sorption sites are not available in a finite mass of sorbent. Thus, at a sufficiently high concentration even a linear isotherm must deviate from its linear trend, eventually levelling off when all sorption sites are satisfied. The range of concentrations over which sorption may appear linear will depend on the solute characteristics and the nature of the sorption sites.

Since the phenol sorption constant $1/n$ is considerably less than one, a greater proportion of solute is sorbed from lower concentration than higher concentration solutions. For example, from Figure 1, when $K = 2.5$ the equivalent linear values of K_d for equilibrium solutions of 30 and 3 mg/L, respectively, are 0.44 and 1.04 mL/g.

The non-linearity of the isotherms implies that, unlike species that sorb linearly, the extent of migration of a dissolved species at any given time will be dependent on the magnitude (and history) of the source concentration. To illustrate this, an updated version of POLLUTE (Rowe and Booker, 1990) was used to generate C/C_o plots vs depth for three different source concentrations, C_o , of 1, 5 and 50 mg/L (Figure 2). The three dashed profiles for $t = 20$ annum yield increasing depths of migration as C_o increases from 1 to 50 mg/L. For all three curves $K = 2.5$ which means K_d decreased from ~ 1.7 to ~ 0.4 with increasing C_o . For assumed linear adsorption with $K_d = 2.5$, the solid C/C_o profile is generated for all values of C_o at $t = 20$ a. It is clear from comparison to the dashed curves that this assumption does not model phenol very satisfactorily.

Actual field profiles for phenol are available for the LaSalle Road landfill, however, they are severely elbowed which means other processes such as biodegradation may be operative (Mucklow, 1990). These curves will be shown as part of the oral presentation.

CONCLUSIONS

Batch tests were conducted using aqueous phenol solutions mixed with natural clayey soil. The major conclusions are as follows:

1. The sorption of phenol on this natural clayey soil is a non-linear function of the porewater concentration, resulting in K_d values as high as 3 mL/g and as low as 0.5 mL/g as the equilibrium solution concentration was varied from 0.5 mg/L to 100 mg/L.
2. Use of non-linear isotherms when modelling diffusion profiles should result in better predictions of the distance of phenol migration.

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REFERENCES

- Allison, L.E., 1965. Organic carbon. In Methods of Soil Analysis, Part 2 (Eds. C.A. Black et al.), American Society of Agronomy, pp. 1367-78.
- Banerji, S.K., K. Piontek and J.T. O'Connor, 1986. Pentachlorophenol adsorption on soils and its potential for migration into ground water. In Hazardous and Industrial Solid Waste Testing and Disposal: Sixth Volume (Eds. D. Lorenzen, R.A. Conway, L.P. Jackson, A. Hamza, C.L. Perket, W.J. Lacy), ASTM STP 933, American Society for Testing and Materials, Philadelphia, pp. 120-39.
- Hamaker, J.W. and J.M. Thompson, 1972. Adsorption. In Organic Chemicals in the Soil Environment (Eds. C.A.I. Goring and J.W. Hamaker), Marcel Dekker, Inc., NY, pp. 49-144.

- Johnson, R.L., J.A. Cherry and J.F. Pankow, 1989. Diffusive contaminant transport in natural clay: a field example and implications for clay-lined waste disposal sites. *Environmental Science and Technology*, Vol. 23, pp. 340-349.
- Karickhoff, S.W., D.S. Brown and T.A. Scott, 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Research*, Vol. 13, pp. 241-248.
- Morrill, L.G., B.C. Mahilum and S.H. Mohiuddum, 1982. Organic Compounds in Soils: Sorption, Degradation and Persistence. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, 326 p.
- Mucklow, J.P., 1990. Phenol migration by diffusion below landfills in natural clayey soils. M.E.Sc. Thesis, Faculty of Engineering Science, The University of Western Ontario, London, Canada.
- O'Connor, D.J. and J.P. Connolly, 1980. The effect of concentration of adsorbing soils on the partitioning coefficient. *Water Research*, Vol. 14, pp. 1517-23.
- Rowe, R.K. and J.R. Booker, 1990. POLLUTE V5.0 - 1D Pollutant Migration Through a Non-Homogeneous Soil - Users Manual. Geotechnical Research Centre, University of Western Ontario, Report No. GEOP 90-1.
- Voice, T.C., C.P. Rice and W.J. Weber, 1983. Effects of solids concentration on the sorptive partitioning of hydrophobic pollutants on aquatic systems. *Environmental Science and Technology*, Vol. 17, pp. 513-18.
- Zytner, R., N. Biswas and J.K. Bewtra, 1989. Adsorption and desorption of perchloroethylene in soils, peat moss and granular activated carbon. *Canadian Journal of Civil Engineering*, Vol. 16, pp. 798-806.

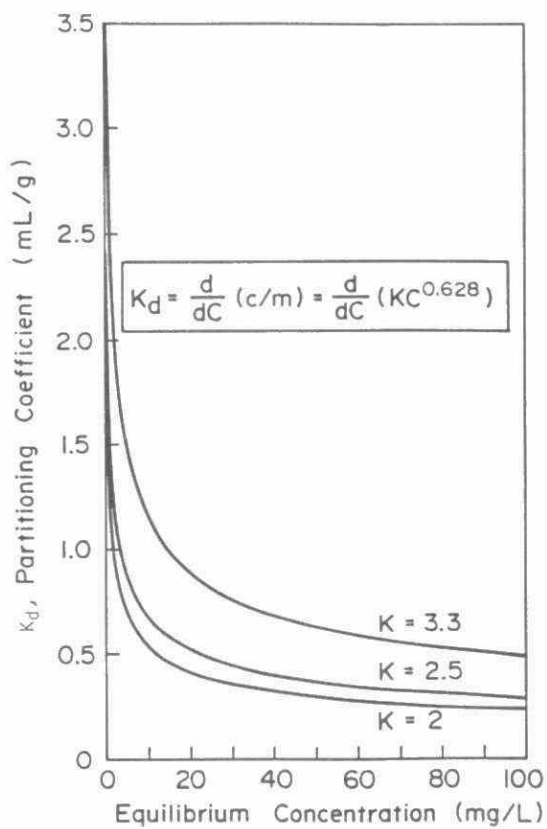


FIGURE 1. PHENOL PARTITIONING COEFFICIENT, K_d

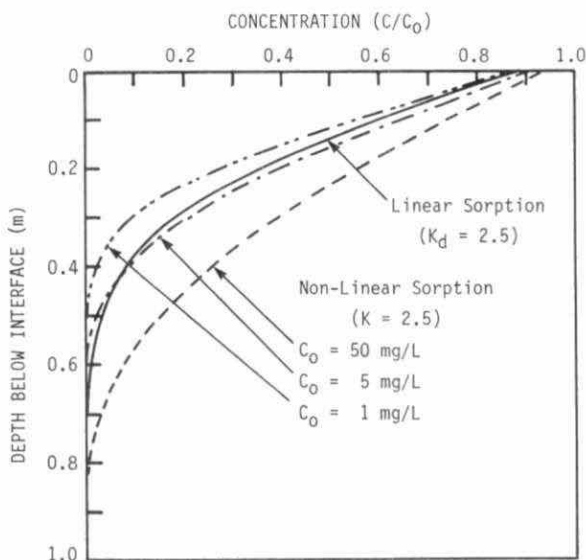


FIGURE 2, RELATIVE CONCENTRATION PROFILES GENERATED BY POLLUTE TO COMPARE EFFECTS OF LINEAR AND NON-LINEAR SORPTION

Test Conditions: $D = 5.3 \times 10^{-6} \text{ cm}^2/\text{s}$; $n = .38$;
 $\rho_d = 1.713 \text{ g/cm}^3$; $t = 20a$; $H_L = 7 \text{ m}$;
 $C_{\text{background}} = 0$

Boundary Conditions: Upper \rightarrow Finite Mass of Contaminants;
 Lower \rightarrow Infinite Bottom Layer

Estimating Landfill Leachate and Contaminant Production

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ABSTRACT

In a landfill, the start of leachate production and contaminant release does not wait until the last green garbage bag has been delivered. It begins the day the first one arrives. It does not remain constant in time nor is it the same for all areas of the site.

The purpose for the work was to develop a rational means for estimating the variable contaminant production that occurs within a landfill throughout its entire life. Discerning the leaching history of one area from that of another was the goal of the research.

The 'Contaminant Estimation in Landfill Leachate' (CELL) model was developed for this purpose. It employs contaminant release curves which calculate the mass of contaminant released as a function of the volume of leachate passing per unit mass of waste.

Estimates of leachate flows used in the CELL model were generated using a modified version of the HELP model developed in this research. This modified method predicts an earlier first appearance of leachate than does the standard application of the model. The rate of site construction and precipitation determine when it appears. Tests using hypothetical landfills indicated that the modified HELP model can be applied successfully to both the construction period and the post closure period of a landfill.

The estimate of contaminant production using the CELL model compared well in both magnitude and pattern with the general trends observed in the field. The model should be upgraded to consider the variability in the initial amounts of contaminants in the waste.

INTRODUCTION

In a landfill, the start of leachate production and contaminant release does not wait until the last green garbage bag has been delivered. It begins the day the first one arrives. The production and contamination of the leachate that begins during the early stages of landfill construction continues for many decades beyond the closure date. Both the leachate quantity and quality produced over this period are dependent on many factors and recently, efforts have been made to model the leaching process.

In current landfill design practice, the computer programs used for estimating the quantity of leachate produced do not include the time it takes to build the landfill up to final cover in the time frame of the simulation. The simulation period generally starts from the time the landfill is near completion. As a result, the leachate production occurring during construction cannot be estimated. Furthermore, the leaching history during this period determines the initial conditions of the landfill which are needed as input for the start of the computer simulations.

The production of contaminant is similar to leachate quantity in that contaminant production occurs during the entire life of the site. However in terms of computer models there are no acceptable models available to simulate contaminant production over this period. The original impetus for the study was to develop such a model, a leachate quality model, but it was soon realized that estimates of the quantity of leachate produced during construction were needed first. The reason for this is that the controlling variable for the proposed contaminant release model was the volume of liquid passing through the waste. This concept is a continuation of work done by McGinley and Kmet (1984), Farquhar (1987) and Reitzel (1990).

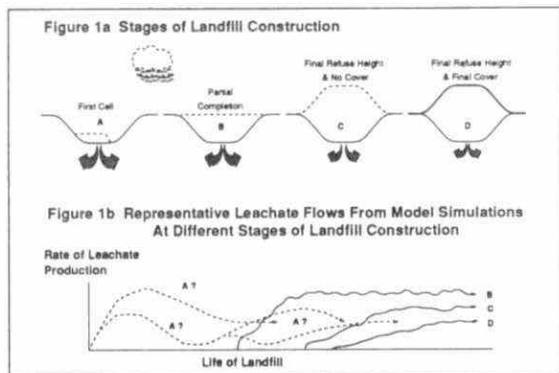
This paper focuses on the methods developed for estimating leachate quantity during construction and post closure

periods. An introduction to the aspect of leachate quality is also included. A second paper covers the leachate quality problem in more detail.(Jarvis & Farquhar 1990)

THE HELP MODEL

The Hydrologic Evaluation of Landfill Performance (HELP) Model is the latest development in the short series of models for solid waste landfill simulation.(Schroeder *et al.* 1984) It represents an attempt to model many of the hydrologic phenomena that take place in and above an landfill all in one package. The HELP model is currently the best of the models available for landfill simulation. At this point it should be noted that the model uses English units and therefore, the results for this study are also presented in English units.

The start of a standard simulation is typically at the point when the final refuse height has been reached and/or when the final cover layer is complete. Figure 1a illustrates the growth of a landfill. The last three stages indicated by the letters B, C and D are the points at which the HELP model can be used to simulate leachate production. Figure 1b is a graphical sketch of what the corresponding leachate production curve might look like from each of the three simulations.



The differences between the curve show the effect of such large time increments between simulation. It is possible to simulate a site at any refuse depth, but long term simulations of sites that have a majority of the waste in place are most common. The main reason for this is that the HELP model algorithm is not designed to simulate the changing dimensions of the landfill during construction. Also, landfill designers are often interested in long term steady-state leachate production for the purpose of comparing different design alternatives.

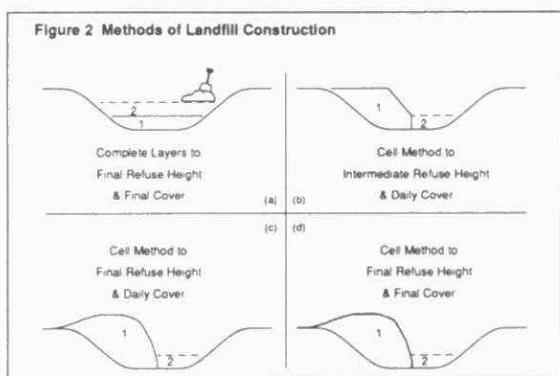
There are two shortcomings associated with this gap in the simulation period, the first one has an important influence on the second. The shortcomings are:

- 1) a significant amount of the early leachate production is not accounted for and,
- 2) the amount of contaminant released during this period cannot be identified without knowing the amount of leachate flowing through the waste.

This first point is important because leaching occurs during this early period when the waste is exposed to direct

precipitation, the runoff is low and the waste depth is shallow. This period is represented as stage A on Figure 1. The manner in which the landfill is constructed in going from stage A to B affects the amount and rate of leachate production which are illustrated by the dotted lines in Figure 1b. Each of these three dotted curves represents a different method of landfill construction.

Figure 2 highlights the different methods of landfill construction which have a direct impact on the rate and amount of leachate production. The first landfill, Figure 2a, shows the landfill being constructed layers until the final refuse height is reached. Each layer covers the entire area of the site. The remaining landfills use the cell method of construction. In Figures 2b and 2c, the refuse is placed in a section of the landfill up to the final height. Subsequent waste is then placed in adjacent areas in a similar manner. Figure 2d represents the case in which the waste is constructed to some intermediate height after which construction continues in an adjacent cell.



The amount of leachate produced over this early stage determines the amount of contaminant released or conversely the amount of contaminant remaining. It is important to know the leaching potential of the waste at different times for the design of efficient leachate treatment facilities. Therefore, the estimates of leachate flow generated in a standard HELP simulation are not adequate for estimating the release of contaminants in a landfill at any point in its life.

The major part of this research consisted of modifying the HELP model to simulate the construction of a municipal solid waste (MSW) landfill. Furthermore, the results of this new method would be compared to standard simulations and to trends in leachate production found in practice. For example, the first leachate from a landfill appears sooner than predicted by the HELP model and thus, the intention was to modify the model to account for this.

HELP MODEL MODIFICATIONS

A standard HELP model simulation of a landfill requires information from three categories, they are: climatologic data, design specifications and soil characteristics. Rather than redesign the entire HELP model, the approach taken was to divide the entire landfill into small areas for simulation and to modify the input data for each of these areas. The following summarizes the main ideas behind the method. A detailed explanation of the procedure can be found elsewhere.(Jarvis 1989).

1 DESIGN SPECIFICATIONS

For each area of a site to be modelled, a series of short simulations are performed; each one in the series spans a discrete time interval in the construction of the landfill. The results of all these short simulations are linked together to form the complete leachate production history.

The design specifications for each simulation can be thought of as a numerical snapshot of the waste in time as the area is being constructed. The only difference between the snapshots is the depth and moisture content of the waste.

2 WASTE AND SOIL CHARACTERISTICS

In order to link the results of these simulations together, a modification of the HELP model was required to ensure continuity in the water budget from one simulation to the next. Typically, at the start of the simulation the moisture content of each layer (soil and waste) are initialized to a value which is either specified by the user or set to default values by the program. At the start of the simulations for the modified approach, the initial moisture contents of the lower soil and waste layers must be set equal to their respective final values at the end of previous simulation. The HELP model code was edited to output the soil moisture levels at the end of each simulation period.

3 COMBINING THE RESULTS

The final modification of the HELP model involved editing the code to generate a separate file for the leachate flow values alone. One point should be clarified here. The HELP model divides the leachate flow at the base of the landfill into lateral drainage and vertical percolation through the liner. The code was modified to recombine these two flows so the total amount of leachate exiting the waste itself is output into a file. This combined value was needed for the calculations of contaminant production.

AN EXAMPLE LANDFILL

To illustrate the above modifications of the HELP model, an simple landfill example was developed. Although the precipitation, landfill geometry and type of construction for the hypothetical case has been simplified, the method can be applied to any situation.

1 THE SITE

A small landfill was comprised of three 4m waste layers which required four months each for placement; placement of the first layer began in January 1990, the second in May 1990 and the third in September 1990. This scenario represents the construction of waste to an intermediate height after which, the incoming waste is deposited in an adjacent area starting at ground level.(Figure 2b)

The first analysis of the site used the conventional application of the HELP model with all three layers in place in September 1990. The simulation was run from September 1990 for five years to the end of 1995. This is a typical application of the HELP model.

The second analysis used the modified form of the model. The simulation period was extended to include the initial construction period from January to September. In both cases, the site remained open (no final cover) for the entire simulation period. Furthermore, because the site was open, no runoff was permitted from the site.

The precipitation data used for both cases was a simplified three phase cycle repeated for each year of the simulation. The first phase extended from February to May with an average of 7.5 in./month (190 mm/month), the second phase from June to September with an average of 1.2 in./month (30 mm/month) and the last phase from October to January with an average of 3.9 in./month (100 mm/month).

2 MODIFIED HELP SIMULATIONS

For the second analysis using the modified HELP model, three simulations were required for the construction period; each one spanned the time period that each of the three layers was exposed (prior to being covered by the next waste layer). Defining the limits for these periods was difficult. The actual placement of the refuse is a continuum of activity; each lift takes time to grow to completion and is not instantly covered when the next layer is started. Some limit had to be decided upon as to how many simulations would be used to model the growth of the waste. Thus, it was assumed that the entire depth of waste for each lift was placed instantaneously for the start of the simulation period.

The results of the three simulations are in the form of three leachate flow profiles. These four month segments of leachate flows were linked in sequence to form the leachate profile for the entire first year of the construction.

3 INITIAL CONDITIONS

Standard Simulation

For the first analysis which used the standard application of the HELP model, the initial soil moisture condition for all three of the waste layers was set equal to 0.2754 (vol./vol.). This is the default value for a standard HELP model application.

Modified Simulation

For the second analysis only the topmost layer was assigned the default initial soil moisture content. The default value was used for the purpose of comparison in this research. Further work should look at the season the layer was placed and adjust the content accordingly. For example, if a layer was constructed during the spring, a slightly higher initial soil moisture would be expected.

Therefore, for the first simulation, the first layer started with an initial soil moisture contents of 0.2754 (vol./vol.). At the start of the next simulation in May, the initial moisture content of this first layer was changed to the value output for the layer in April and the initial moisture content of the second (new) layer was set to the default value.

This process was repeated for the third simulation. The last step was to continue the simulation for an additional five years to the end of 1995. At the start of this final simulation the soil moisture contents for the three layers were adjusted to their respective values at the end of December 1990 to maintain the water budget balance.

4 RESULTS FOR THREE LAYERS

The results of these two analyses are shown in Figure 3. Leachate first appears earlier with modified approach than it does with the conventional application. In the modified approach, the first significant amount of leachate appears in March 1990 whereas in the standard application it does not begin until the latter half of 1991. This is consistent with field observations.

5 EXTENDING TO NINE LAYERS

The second step in this investigation was to repeat these two analyses on a section where the construction continued to final refuse height.(Figure 2c) Rather than stop at three layers the site was extended to nine layers which took three years to construct. Again, the first layer was placed in January 1990 but the final layer was not placed until September 1992. Therefore, in the standard application of the model, the simulation began in September 1992 and was carried out to the end of 1999. In the modified analyses, the simulation period covered the first three years of construction and extended for a period of seven years past construction to the end of 1999.

Figure 3 Monthly Leachate Production From Three Layers of Waste With Initial Moisture Content = 0.2754

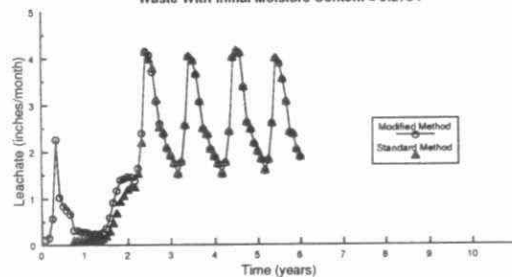


Figure 4 Monthly Leachate Production From Nine Layers of Waste With Initial Moisture Content = 0.2754

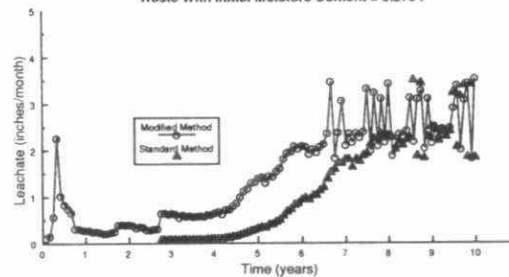


Figure 5 Cumulative Leachate Production From Nine Layers Using 2 Methods & 2 Initial Moisture Contents

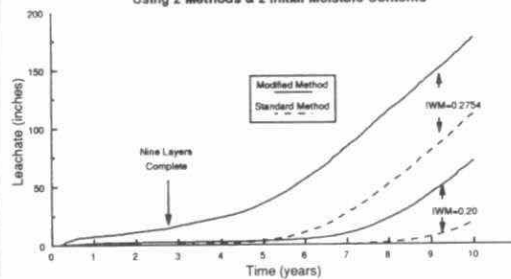
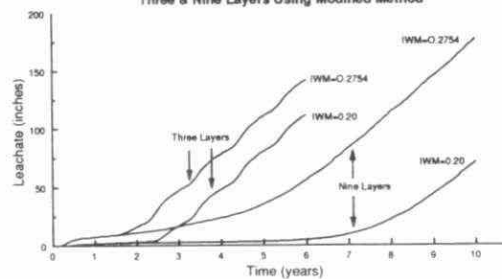


Figure 6 Cumulative Leachate Production From Three & Nine Layers Using Modified Method



The same precipitation cycle that was used for the three layer study was used in this part of study. Also, the depth of the layers remained at 4 m and the same pattern was used for constructing the waste; January to April, May to September and October to December.

The results of the two analyses on the nine layer test site are presented in Figure 4. The diagram shows the leachate production resulting from the two approaches to modelling the waste layers. In the standard case, significant leachate production did not begin until the end of 1994. Steady-state production, fluctuating seasonally but averaging approximately 3 in./month, was achieved in 1998.

For the modified approach, leachate first appeared within the first year (1990) for a short period and continued throughout the construction period at a rate of approximately 0.5 inches/month. Leachate production began to increase steadily once all the layers were in place (end of year three). Steady-state production (approximately 3 in./month) was achieved at the end of 1996, two years earlier than the standard case.

Figure 5 shows the cumulative leachate production for the two cases (top two lines). By the time the standard simulation was started, the modified case had predicted approximately 20 inches of leachate production. By the end of 1995 the modified method had estimated 50 inches more leachate than the standard method and 70 inches more by the end of the tenth year. Because both cases had achieved steady-state at the end of the ten years, this difference of 70 inches would stay constant. However, the difference between contaminant concentrations would not be.

In all cases, the final steady-state rate of leachate production would be reduced if a final cover were constructed.

6 EFFECT OF DRY WASTE

To examine the effect of *drier* waste layers, the above simulations were repeated with the default value of 0.2754 (vol./vol.) for the initial waste moisture (IWM) content lowered to 0.20 (vol./vol.). Again, in the modified cases only the top layer was assigned this value; the values for the lower layers were assigned the correct values to maintain the water budget. For the standard application, all the layers were assigned the initial moisture content of 0.20 (vol./vol.).

As expected, the early rate of leachate production was lower for the dryer waste scenario. Figure 5 shows the cumulative leachate production for the two methods for both the high and low IWM contents. In both cases, the modified method produced more leachate than the standard case at each level of initial moisture content. Even the modified method at low initial moisture predicted approximately 2 inches of leachate production before the standard method even started.

7 IMPACT OF DIFFERENT CONSTRUCTION METHODS

The effect of different methods of construction is evident in the comparison of the results of leachate production in the first five years for the three and nine layer cases. The three layer case represents lateral construction; the three layers are placed and then construction begins again at ground level in an adjacent area. The nine layers represents vertical construction toward final refuse height.

Figure 6 represents the cumulative leachate production for the three and nine layer cases at the two levels of initial moisture content. As expected, for a given initial moisture content the open three layers produced more leachate by the end of the first five years than did the nine layer case. In the nine layer case, more of the infiltration was diverted to saturating the rapidly growing column of waste. Thus, vertical construction is preferable for reducing total leachate production.

Prior to the end of year three, the leachate production for the nine layer-high IWM case exceeds that of the three layer-low IWM case. Beyond this point, the opposite holds true. This illustrates how the rate of vertical construction can affect the rate of leachate production. If the nine layers were placed at a slower rate, each layer would have more time to become saturated and the entire column would reach steady-state earlier. The result on the graph would be that the nine layers-high IWM curve would approach a shape similar to the shape of the three layers-low IWM curve. From these results, it is the case that, for a given rainfall rate, both the rate of vertical construction and the initial waste moisture determine the profile of the leachate production.

Finally, the graph also illustrates how the additional layers damp out the effect of the seasonality in precipitation on the production of leachate. The seasonal fluctuations are more evident in the three layer case.

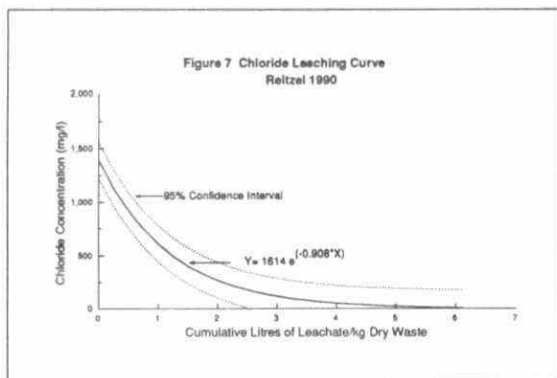
In this simplified case, the results are expected. However, in reality the possibility that each layer has a different initial moisture content explains the highly variable nature of the early leachate production. This could be modelled by assigning initial moisture contents according to the season in which the waste was deposited.

CONTAMINANT PRODUCTION

In recent years, attempts have been made to characterize the quality of leachate based on a number of independent variables. The most common has been the age of the waste. (Wigh 1984, Lu *et al.* 1984) The difficulty with using the age of the waste is that, for 20 year old waste for example, the remaining leaching potential of the waste is considered to be the same regardless of whether it is located in a dry climate or in a wet climate.

More recently, research by McGinley & Kmet (1984), Farquhar (1987) and Reitzel (1990) has investigated the leachate quality as a function of the volume of liquid passing through the waste. It can be thought of as a rinsing effect. Thus, waste stored in a wet environment will have a higher contaminant production in the earlier years than will a waste which is stored in a dryer climate.

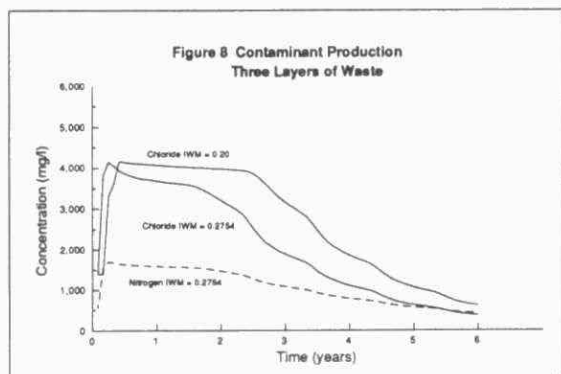
Figure 7 is an example of the curve developed for chloride in the research by Reitzel (1990); the equation for the curve is also given. The seven contaminants that were investigated included: chloride, nitrogen, phosphorous, iron, lead, cadmium and COD.



While this paper focuses on the research into leachate quality, subsequent work was carried out to incorporate the

work of Reitzel (1990) into a model which will predict the leachate quality in a landfill. The model is called the 'Contaminant Estimation in Landfill Leachate' (CELL) model (Jarvis 1989).

To give the reader an idea of the results of this work, the CELL model was applied to the example used to illustrate the leachate quantity research. Figure 8 shows the results for chloride and ammonia for the three layer site. Figure 8 also illustrates the effect of a dryer (TWM = 0.20 vol./vol.) and a wetter (TWM = 0.2754 vol.vol.) environment on the production of contaminant. In the wetter environment, more of the contaminant is flushed out of the waste earlier in time.



CONCLUSIONS

The results from this study indicate that, by modifying application of the HELP model to reflect the actual construction history of the waste, the resulting leachate patterns better reflect what is actually found in the field. Leachate production begins when the first layer is constructed and may or may not continue throughout construction depending on the other factors included in this study; type of construction, rate of construction and the initial waste moisture content.

The effect of different construction methods is that vertical construction, as opposed to lateral, reduces the total amount of leachate produced.

The analysis also revealed that the rate of vertical construction had an effect on the continuity of the production of leachate. The slower the layers are placed, relative to a fixed rainfall, the more likely a steady flow of leachate may continue from the time it first appears. The topmost layers have more time to reach field capacity by direct precipitation before a dryer layer covers them. A faster filling rate will result in a more fragmented flow profile and lower total leachate production.

The combined effect of the initial waste moisture content, fill rate and precipitation lead to the conclusions that there is no simple way to estimate the first appearance of leachate based on waste depth alone. Leachate flow can be reduced by rapid vertical landfill construction so that infiltration does not exceed the growth of in field capacity.

The introduction to the leachate quality at the end of this paper illustrates the impact of leachate quantity on leachate

quality in a landfill environment. This information can assist in many areas such as the modelling of contaminant migration through a liner towards the groundwater and in the design of leachate treatment facilities.

REFERENCES

Farquhar, G.J. (1987) "Leachate: Production and Characterization", In Proceedings of The Canadian Society for Civil Engineering Centennial Conference, Montreal May 19-22, 1987.

Jarvis, L.A., (1989) "Estimating Landfill Leachate Contaminant Production", MASC Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1989.

Jarvis, L.A. and Farquhar, G.J., (1990) "A Method to Predict Landfill Leachate Contaminant Levels", University of Waterloo, Waterloo, Ontario, (Paper in progress).

Lu, J.S.C., Eichenberger, B. and Stearns, R.J., (1984) "Production and Management of Leachate from Municipal Landfills: Summary and Assessment", Calscience Research, Inc., Huntington Beach, CA, Prepared for the Municipal Environmental Research Laboratory, U.S. Environmental Agency, Cincinnati, Ohio, May 1984.

McGinley, P.M. and Kmet, P., (1984) "Formation, Characteristics, Treatment and Disposal of Leachate from Municipal Solid Waste Landfills", A Wisconsin Department of Natural Resources Special Report.

Reitzel, S.F. (1990) "The Temporal Characterization of Municipal Solid Waste Leachate", MASC Thesis, University of Waterloo, Waterloo, Ontario, Canada, 1990.

Schroeder, P.R., Gibson, A.C. and Smolen, M.D., "The Hydrologic Evaluation of Landfill Performance (HELP) Model Volumes I & II Documentation for Version 1", U.S. Army Engineer Waterways Experimental Station, Vicksburg, MS, Prepared for the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1984.

Wigh, R.J., (1984) "Landfill Research at the Boone County Field Site", Regional Services Corp., Inc., Columbus, IN, Prepared for the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February, 1984.

Test of a Chemical Mechanical Process for the Decontamination
of Non-Anatomical Biomedical Waste

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INTRODUCTION

Hospitals in the Metropolitan area produce an estimated 4.4 million pounds of yellow bag waste each year. Yellow bag hospital waste may consist of non-anatomical materials such as gauze, paper, swabs, plastics, syringes and needles, as well as lab cultures.

Studies have been initiated to examine methods of disposal of this biomedical waste; one process currently under investigation is the hammermill shredding/disinfection system. In the hammermill disinfection process the bags are coarsely shredded and concurrently sprayed with a solution of sodium hypochlorite. A high speed hammermill subsequently breaks the shredded waste into smaller particles. The wet mixture is then fed onto a perforated belt conveyor and the solid residue is dewatered before transportation to a disposal site. The liquid portion is separated for discharge into the municipal sanitary sewer.

The objective of this paper is to present an approach for evaluating the ability of the mechanical disinfection process to decontaminate biomedical waste. Emphasis will be placed on the following aspects of the evaluation: a) investigation of the effectiveness of disinfection using varying chlorine concentrations with different pH conditions and contact times; b) comparison of the inhibition of different species of the same bacterial genus by chlorine; c) development of a method for isolating viruses from untreated and treated hospital waste; d) comparison of desorption methods to recover bacteria that are adsorbed to crushed waste; and e) examination of the bactericidal activity of chlorine and Virkon on *P. aeruginosa* in crushed waste.

MATERIALS AND METHODS

Mechanical Crushers

The Medical Safe TEC Z-12, 500 Infectious Waste Disposal System grinds the waste to a granular size using a pre-shredder and a hammermill and simultaneously treats it with a disinfectant solution. The dry weight of the machine is approximately 4, 536 Kg.

The machine was not in operation when the study was initiated and therefore a smaller crusher, the Bio-Nurbel 100, was used in the investigation.

The Bio-Nurbel 100 Mechanical Waste Disinfecting and Disposal System uses a three blade crusher and mount system to grind materials such as glass, hard plastics, syringes and needles. A disinfectant is sprayed onto the material during the crushing of the waste. The dry weight of the machine is 100 Kg.

Disinfectants

The stock chlorine solution used as a disinfecting agent was 6% sodium hypochlorite. At the completion of each experiment, the chlorine was neutralized with sodium thiosulphate according to the reaction: $2\text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl}$.

The virucidal agent, VirkonTM, was employed as a 2% solution. Since the neutralizing agent for Virkon has yet to be determined, the disinfectant was neutralized by dilution at the conclusion of each experiment.

Factors Affecting Chlorine Disinfection

The bactericidal effect of chlorine on *Pseudomonas aeruginosa*, *Serratia marcescens*, *Mycobacterium phlei*, *M. smegmatis*, *Bacillus subtilis* and *B. megaterium* was assessed using the methods described by Seyfried and Fraser (1980). Chlorine demand-free buffered water (CDBF) at pH 4.0, 5.0, 9.0 and 10.0 was used for all dilutions and assays. Glassware was acid washed, treated overnight with a 10mg/L sodium hypochlorite solution, rinsed with chlorine-demand-free water (APHA, 1989) and sterilized with hot air. The stock solution of approximately 10,000 mg/L free chlorine was kept refrigerated in the dark. The chlorine concentration was determined using the DPD colorimetric method (APHA, 1989).

The bacterial cultures were centrifuged and washed twice with CDBF adjusted to the appropriate pH. A 1.0 mL aliquot of culture and 1.0 mL of sodium hypochlorite (0.1 to 1000 mg/L) were added to 8 mL of CDBF. At time intervals of 1, 30, 60 and 120 min, 1 mL samples were removed and neutralized with sodium thiosulfate solution. Controls and test solutions were diluted and plated to determine the CFU/mL.

Elution of Viruses from Crushed Waste

The virus used was polio type 1, containing 100 TCID₅₀/0.1 mL (10^{-7}) with HBSS pH 7 as diluent. Freshly trypsinised vero cells diluted in growth medium (1.3×10^6 cells/mL) and 24 h monolayers of vero cells in 24-well plates were the tissue cultures employed in the study. The washing/eluting agents included HBSS pH 7, HBSS pH9, Tryptose Phosphate Broth pH9, 3% Beef extract and 1% non-fat dry milk in 0.05 M glycine. The negative stain used for electron microscopy examination was 2% phosphotungstic acid.

Wash/elution Method

A 4g amount of sterile simulated crushed hospital waste was placed in each of three flasks and 40mL of the virus dilution was added. The flasks were left at room temperature with frequent, gentle agitation for 90 min. The fluid was then harvested and replaced with 40mL of one of the washing/eluting agents. After 5 min, with gentle agitation at 1 min intervals, these fluids were harvested, and, using sterile forceps, approximately one-tenth of the crush was removed and added to a tissue culture tube containing 4mL of the tissue culture cell suspension. The washes were repeated for a total of 10 times, using 40mL of fluid for each wash and harvesting a tenth of the crush with clean, sterile forceps after each wash.

Co-Cultivation Method for Testing for Presence of Virus on Crush

The harvested crush was added to 4mL of the cell suspension in tissue culture tubes. The tubes were incubated in a slanted position and examined daily. Within 24 h a monolayer of cells formed, with the subsequent appearance of a cytopathic effect within a few days if virus was present. Control tubes, containing untreated crush and the cell suspension were included. The monolayer formed within 24 h, but there was no cytopathic effect after further incubation.

Testing of the Washes

The ten washes collected from each of the washing/elution agents used were tested by inoculating 0.1mL of each into 4 cell monolayers in a 24 well plate. After 1 hr adsorption at 37°C, maintenance medium was added to each well. Controls included monolayers inoculated with each of the wash/elution agents, and uninoculated cell controls. All plates were incubated in a humidified CO₂ incubator and examined daily.

Recovery of *P. aeruginosa* from Crushed Waste

The waste used was pre-ground plastic material, including syringes, that had been sterilized by autoclaving. The bacterial culture was *P. aeruginosa* grown in Nutrient Broth (Gibco) for 24 h at 35°C. The mechanical methods of desorption included blending, shaking, and sonication. For the blending experiments, 5g of crushed waste was added to 45mL of sterile saline in a

sterilized blender and blended (liquefy setting) for 2 min. Shaking included placing 5g of waste in a bottle with 45mL of saline and shaking vigorously for 2 min. For sonication, 1g of waste was placed in a sterile test tube and 9mL of saline was added. The material was sonicated for 1 min, vortexed, and then sonicated for another min. Vortexing of the sample was then carried out periodically for 30 min to allow the organisms to recover.

At the beginning of each experiment, a plate count was made of the 24 h culture of *P. aeruginosa* to determine the CFU/mL. A 300mL volume of *Pseudomonas* culture was added to a sterile beaker containing 350g of the sterilized waste; the bacteria and waste were then thoroughly mixed. Grab samples were taken as follows: A, C, F and H from the top of the waste in the beaker; and B, D, G and I from the bottom of the beaker. An attempt was made to recover the *Pseudomonas* organisms from the liquid material and the solid waste before and after processing in the Bio-Nurbel machine. The desorption methods used on the samples were as follows: solid sample A was blended; solid sample B was shaken; and solid sample C and D were sonicated. The aforementioned solid samples and sample E, collected from the liquid portion of the waste/culture mix, were taken before the bacteria and crushed waste were processed. For processing, buffered peptone water (APHA) with a pH of 7.2 was used in place of a disinfectant in the Bio-Nurbel machine. The machine was allowed to run for 1 min before putting the waste/culture mix through. During processing, the waste was collected in a sterile 4L beaker. Following the crushing treatment, solid sample F was blended, solid sample G was shaken, and solid samples H and I were sonicated. The J sample was taken from the liquid portion of the waste/culture mix. All samples were appropriately diluted in saline and spread plated onto Nutrient Agar (Gibco). The plates were incubated at 35°C for 24 h and the CFU/mL determined. This experiment was repeated three times.

Comparison of Bacterial Desorption Methods

The same procedure was followed as described for the crushed waste recovery study. The bacteria included *Serratia marcescens*, *Staphylococcus epidermidis*, grown in Tryptic Soy Broth (Gibco), and *P. aeruginosa*, cultured in Nutrient Broth (Gibco). Incubation was at 35°C for 24 h. The CFU/mL was determined for each organism and the bacteria were mixed with crushed waste as outlined previously. The waste/culture mix was processed in the Bio-Nurbel system using buffered peptone water instead of a disinfectant. After processing, blending and shaking were used to desorb *S. marcescens* from the crush. *P. aeruginosa* and *S. epidermidis* in the crushed waste were subjected to blending, shaking, and sonication. Enumeration of the desorbed organisms was carried out using Tryptic Soy Agar for *S. marcescens* and *S. epidermidis* and Nutrient Agar for *P. aeruginosa*.

Effect of Chlorine and Virkon on Waste Containing *P. aeruginosa*

The method described for the recovery of *P. aeruginosa* from crushed waste was followed with the samples being analyzed before and after crushing. A 5.0L volume of either 0.2% Cl or 2% Virkon was added to the Bio-Nurbel machine as a disinfectant in place of buffered peptone water.

Sterile saline served as diluent for the Virkon experiments whereas chlorine demand free buffer served as a diluent for the chlorine tests. Each disinfectant was assessed in two separate experiments.

RESULTS AND DISCUSSION

Factors Affecting Chlorine Disinfection

The *S. marcescens* bacteria were completely inactivated by 10mg/L free chlorine after 30 min at a pH of 4 or 5. With a pH of 9, however, 100 mg/L was needed to produce 100% inactivation within the same period.

P. aeruginosa proved to be more sensitive to chlorine than *S. marcescens*. For example, 1mg/L free chlorine produced 100% inhibition of the organism within 30 min at pH 5.

Mycobacteria also were inhibited by chlorine more readily under acidic conditions. A 30 min exposure to 10 mg/L free chlorine completely inhibited both *M. phlei* and *M. smegmatis* at pH4 whereas at pH10, 100mg/L free chlorine was needed.

Young vegetative cells of *B. subtilis* and *B. megaterium* that had not yet produced spores were inactivated by 100mg/L chlorine. However, when *B. subtilis* cultures were heat treated to eliminate the vegetative cells and leave only spores, it was found that 10,000mg/L free chlorine was not sufficient to produce 100% inactivation within 2 h at pH5.

Elution of Viruses from Crushed Waste

When the zero time and 90 min virus samples were titrated only a very slight difference in titre was noted.

The results of the wash/elution method showed that the eluting agents Tryptose Phosphate Broth, Beef extract and non-fat dry milk in glycine were slightly more efficient than the HBSS. However, even after 10 washes with the eluting agents the virus could still be recovered from the crush itself.

The co-cultivation technique proved to be a more effective method of eluting virus from crushed waste. The tissue culture tubes were examined daily and on day one a good monolayer of cells was observed. After four days, a typical enterovirus cytopathic effect could be seen in all samples.

Tables giving details of the aforementioned data are available upon request.

Recovery of *P. Aeruginosa* from Crushed Waste

The results showed that, as long as the crushed waste and bacterial cultures were well mixed, the differences in bacterial recovery from different collection sites in the waste were minimal.

As may be seen in Fig. 1, more organisms were recovered from the liquid portion of the mixture, both before and after processing, than from the crush itself. Blending of the crush appeared to produce a slightly higher recovery of *P. aeruginosa* organisms than shaking and sonication. Similar results were produced from all three trials.

Comparison of Bacterial Desorption Methods

Fig. 2 shows the comparative results of the three desorption procedures. Statistical analysis of the data indicated that only the tests using *S. marcescens* yielded a significant difference between blending and shaking techniques.

Previous studies on bacterial adsorption to sediment (Seyfried and Owen, 1979) indicated that if weighed amounts of sediment were added directly to MPN tubes containing appropriate recovery media, the adsorption effect was decreased. Further experiments are planned to study bacterial recovery from crushed waste using the MPN method.

Effect of Chlorine and Virkon on Waste Containing *P. aeruginosa*

P. aeruginosa, mixed with crushed waste, was treated in the Bio-Nurbel machine with 0.2% chlorine or 2% Virkon. Both disinfectants produced 100% inhibition of *P. aeruginosa*, as shown in Figs. 3 and 4. The results from duplicate experiments were similar.

P. aeruginosa, an opportunistic pathogen, is the causative agent of nosocomial infections. It was incorporated in this study because it is an important organism in a hospital setting. However, it should be noted that *P. aeruginosa* is relatively chlorine sensitive in comparison with mycobacteria. Future studies are planned to determine the effectiveness of chlorine and Virkon on other bacteria, phage and viruses in crushed waste.

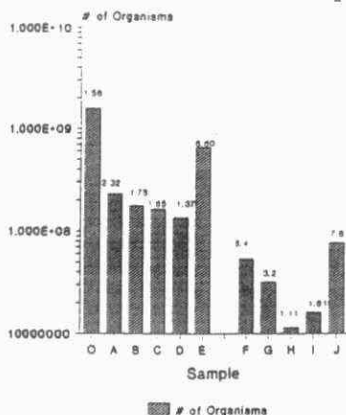


Fig. 1 Comparative recovery of *P. aeruginosa* from crushed waste.

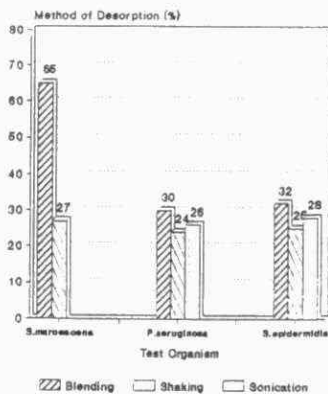


Fig. 2 Bacterial desorption from crushed waste by blending, shaking, and sonication.

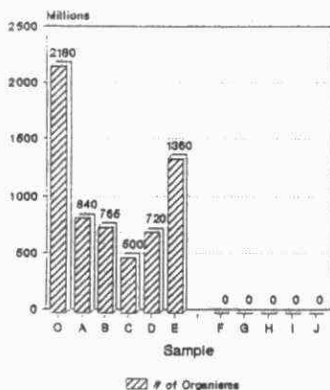


Fig. 3 Effect of chlorine on *P. aeruginosa* in crushed waste.

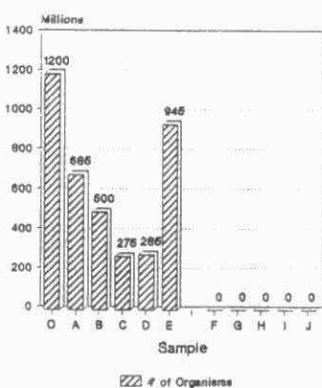


Fig. 4 Effect of Virkon on *P. aeruginosa* in crushed waste.

LEGEND Sample O = pure culture; samples A to E = before processing; Samples F to J = after processing; A and F = blended; B and G = shaken; C, D, H and I = sonicated; F and J = liquid.

SUMMARY

The effect of chlorine on a pure bacterial culture was tested and it was found that P. aeruginosa was the most sensitive to free chlorine; the spores of B. subtilis were the most resistant. Different species of the same genus demonstrated similar susceptibilities to chlorine. Lowering the pH and increasing the chlorine concentration and exposure time improved the inhibitory action of chlorine.

The co-cultivation technique was shown to be better than the wash/elution method for the recovery of virus from crushed waste.

Blending, shaking and sonication were used to facilitate the recovery of S. marcescens, P. aeruginosa, and S. epidermidis from crushed waste that had been processed in the Bio-Nurbel machine with buffered peptone water in place of a disinfectant. It was shown that, both before and after processing, a higher level of organisms could be recovered from the liquid than from the crush.

One hundred percent inactivation of P. aeruginosa was achieved when the organism was mixed with crushed waste and treated with either 0.2% chlorine or 2% Virkon in the Bio-Nurbel machine.

REFERENCES

- American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. 17th ed. American Public Health Association, Inc., New York, NY.
- Seyfried, P.L. and D.J. Fraser. 1980. Persistence of Pseudomonas aeruginosa in chlorinated swimming pools. Can. J. Microbiol. 26: 350-355.
- Seyfried, P.L. and A.R.G. Owen. 1979. Evaluation of the most probable number technique for the enumeration of fecal coliforms and Pseudomonas aeruginosa in sediment. In Methodology for Biomass Determination and Microbial Activities in Sediments. American Society for Testing and Materials, STP 673, C.D. Litchfield and P.L. Seyfried eds., pp. 52-63.

VOLUME II
SESSION C
LIQUID & SOLID WASTE RESEARCH
POSTER PRESENTATIONS

PURIFICATION AND DETOXIFICATION OF TEXTILE DYEBATH EFFLUENT
BY ELECTROCHEMICAL TREATMENT

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INTRODUCTION

Wastewater from the textile industry is detrimental to our environment. Although variable in quantity and composition depending upon the production processes and raw materials used, the wastewaters are commonly characterized by a high organic loading and high solids content. Dyebath effluents are, in addition, aesthetic pollutants and may also impede light penetration in a receiving body of water, thus interfering with vital biological processes. Dye effluents also pose the problem of potentially toxic or carcinogenic chemicals entering sewage treatment facilities not specifically designed for them.

RESEARCH OBJECTIVES

1. To evaluate the efficacy of a commercially available electrochemical cell in decolorizing textile dyebath effluent.
2. To evaluate the ability of the electrochemical cell to reduce the acute toxicity of textile dyebath effluent.
3. To determine whether the electrochemically treated dyebath effluent can be recycled in subsequent dyeing operations.
4. To determine the limit, if any, on the number of times treated dyebath effluent can be recycled.

MATERIALS AND METHODS

1. Four specimens of polyester fabric were dyed with each of three of the disperse dyes commonly used in Canada. The dyeings were originally done using only a levelling agent as an assistant; they were then repeated using the following carriers (which are also commonly used in Canada): (1) Carolid RSN, (2) Carolid NOL, and (3) Carolid MN-ISN.
2. All effluents were electrochemically treated by immersion of an electrochemical cell (0.4 amps 5 plates) in 500 ml of effluent for 8 minutes. Precipitation was accelerated by adding a polyacrylamide precipitator. The precipitated sludge was removed by filtration.
3. The acute toxicity of all untreated and electrochemically treated effluents was determined by Daphnia magna bioassay.

4. The treated effluent was used as water in a second dyeing and the dyed samples were evaluated visually for uniformity. The colour was measured using a Hunterlab Color Quest spectrophotometer and compared to that of the samples dyed using pure water.
5. Determination of the limit on the number of times treated effluent can be used is now in progress. Effluent from each dye-carrier combination is electrochemically treated and filtered prior to reuse in a subsequent dyeing operation with the same dyes and chemical assistants.

RESULTS

1. Operation of the cell at 0.4 amps for 8 minutes released sufficient iron to permit optimal removal of residual dyestuff from the dispersed dye effluent. This amount was determined to be 280 mg/l.
2. The acute toxicities of the three dyes, when used in combination with the three carriers, was reduced in all cases. The average decrease in toxicity of dyebaths containing the carriers Carolid RSN, Carolid NOL and Carolid MN-ISN was 186%, 182% and 107%, respectively. The dye Cibacel Yellow-E 4RLF showed an overall greater decrease in toxicity than either of the other two dyes (table 1).
3. The electrochemically treated, filtered effluent which was used for the final dyeings contained substantial amounts of iron but no dyestuff. The specimens dyed with each of the dye-carrier combinations were level with no dyespots, and would be considered commercially acceptable.
4. In general, replicate specimens dyed using fresh water showed less colour variation than did those dyed with recycled effluent. The greater colour variation in the latter specimens is probably due to the presence of iron in the dyebath.
5. The colour difference between the control samples & those dyed using recycled effluent for all dye-carrier combinations was greater than recommended tolerances (table 2). When the effluent was filtered twice prior to recycling, color differences between samples dyed using fresh and recycled liquor were, in most cases, within commercially acceptable limits.
6. Ongoing research indicates that, when Resolin Blue FBL is applied with each of the three carriers, two (Carolid NOL and Carolid MN-ISN) can be used for at least nine dyeings with commercially acceptable colour differences. All dyeings performed using treated effluent containing Resolin Blue FBL/Carolid RSN are beyond commercially acceptable colour limits.

7. Our data indicate that recycling of electrochemically purified, filtered dyebath effluent can give commercially acceptable results provided that dyes and carriers are properly selected. It is likely that each dyebath formula will have to be pre-tested to determine the optimal purification procedure.

SUMMARY

1. The electrochemical treatment used in this research was highly effective in removing colour from the disperse dye effluents tested.
2. Toxicity of the effluent was substantially reduced by the electrochemical treatment.
3. Reuse of the treated effluent resulted in first quality dyeings although there were colour differences in specimens dyed using the fresh and the recycled liquor. The colour differences were markedly reduced by increasing the number of filtration processes.
4. In some cases, treated effluent can be repeatedly reused without adverse effect on the quality of the dyed fabrics.

IMPLICATIONS

The research suggests that electrochemical treatment of dyebath effluent removes colour so that the effluent can be successfully recycled in subsequent dyeing processes. Alternatively, if the effluent is released into the environment, the treatment significantly reduces its acute toxicity.

TABLE 1
SUMMARY OF ACUTE TOXICITY TO DAPHNIA MAGNA OF DYES
BEFORE AND AFTER ELECTROCHEMICAL TREATMENT

Dyestuff	Carrier	LC ₅₀		% Decrease in Toxicity
		Before Treatment	After Treatment	
Resolin Blue FBL	Carolid RSN	35.4	70.7	99.7
Resolin Red FRL	Carolid RSN	27.8	35.4	27.3
Cibacet Yellow E 4RLF	Carolid RSN	12.0	63.7	$\frac{-}{x} = \frac{430.8}{185.9}$
Resolin Blue FBL	Carolid NOL	13.7	21.8	59.1
Resolin Red FRL	Carolid NOL	10.3	31.8	208.7
Cibacet Yellow E 4RLF	Carolid NOL	16.2	61.4	$\frac{-}{x} = \frac{279.0}{182.3}$
Resolin Blue FBL	Carolid MN-ISN	52.6	70.7	34.4
Resolin Red FRL	Carolid MN-ISN	19.9	35.4	77.9
Cibacet Yellow E 4RLF	Carolid MN-ISN	18.0	55.4	$\frac{-}{x} = \frac{207.8}{106.7}$

TABLE 2
COLOUR DIFFERENCES BETWEEN SAMPLES DYED
USING FRESH AND RECYCLED EFFLUENT

Dyestuff	Carrier	Total Color Difference (ΔE)
Resolin Blue FBL	Carolid RSN	3.03
Resolin Red FRL	Carolid RSN	0.71
Cibacet Yellow E 4RLF	Carolid RSN	2.76
Resolin Blue FBL	Carolid NOL	6.08
Resolin Red FRL	Carolid NOL	1.00
Cibacet Yellow E 4RLF	Carolid NOL	7.66
Resolin Blue FBL	Carolid MN-ISN	1.73
Resolin Red FRL	Carolid MN-ISN	1.15
Cibacet Yellow E 4RLF	Carolid MN-ISN	8.11

* 1.00 is considered the maximum ΔE value for commercial acceptability.

STABILIZATION OF A WASTE IN A LANDFILL ENVIRONMENT.

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INTRODUCTION

The use of landfill disposal continues to be the most widely used system for disposal of municipal refuse. Despite the long history of landfill use, the impact of the landfill on the surrounding environment and aquifer remains controversial. Although the initial content of the landfill can be estimated with reasonable accuracy, the rate and extent of material transfer to the environment is not well defined. Part of the difficulty is in quantifying the parameters that control the chemical and biological reactions occurring within the landfill mass. Knowledge of these parameters is critical in determining environmental impact and in improving the design of long term landfill sites.

While field studies of existing landfills provide valuable information, there is little opportunity to modify controlling parameters to quantify their significance. On the other hand, laboratory studies generally have not been able to duplicate field behaviour and thus lack applicability for environmental modelling. This study has employed large scale laboratory leaching columns which were designed to simulate landfill behaviour. There are 16 columns in operation packed with 4 different compositions: 100% municipal solid waste(MSW), MSW + 8% industrial waste(IW), MSW + 30% IW and 8% IW in sand. The high density polyethylene cylindrical columns are 1.93m high, and 0.33m in diameter and contain approximately 43 kg (dry weight) of MSW. One half of the columns receive moisture input from precipitation while the other half receive controlled periodic water additions. The systems are maintained in unsaturated flow conditions with regular leachate removal from the bottom reservoirs. As a result of their size the columns are operated in an outside location. This scale of experimentation, though large for laboratory studies, is required for developing the landfill hydrodynamics and biological activity. The role of hazardous waste was studied using a selected hazardous waste at 8 and 30 weight percent of the municipal refuse content. The waste was added in layers in the test cells. The effect of hazardous waste in a landfill site is not well understood. Several studies have indicated little change of leachate quality with a variety of wastes. A serious concern with hazardous wastes is the long term behaviour in the landfill environment which goes through several phases before final stabilization. The effects of the hazardous wastes may not be apparent until the buffering capacity of the landfill is lost. The leachate quality of a variety of test cells has been studied over an extended period (5 years) and the effects of the hazardous waste addition to the test cells are examined.

RESULTS and DISCUSSION

Previous work has demonstrated that the behaviour of the test cells containing municipal refuse is similar to that observed in medium and large field cell studies. The comparison was based on the concentration behaviour of 8 elements (Cu, Zn, Fe, Na, K, Cl, Mn, Mg), COD and pH. Of interest in this phase of the research is the stabilization of the MSW and of the industrial solid waste.

The industrial waste composition is shown in the table. The waste was very fine and highly alkaline. The Regulation 309 leachate test showed lead solubilization to be above the guidelines.

LEAD

The studies of lead solubilization from the waste disposed in sand columns revealed very high concentrations during the initial 6 months. Over the 5 year period, 6% of the total lead has been leached from the test cells containing sand. Though low levels < 1 mg/l are now found in the leachate, the pH is still alkaline (10).

From test cells containing the same mass of industrial waste but having MSW instead of sand and assuming that only the industrial waste contributed to the lead values, only 0.034% of the lead leached over the same period. For the test cells having a 30% industrial waste loading, the total lead leached was the same but the percent leached was only 0.006%. Test cells having only MSW and no industrial waste have leached twice the amount of lead found from cells with industrial waste. The beneficial effect produced by the industrial waste appears to be related to the alkalinity of the waste.

CADMIUM

The cadmium levels in the industrial waste were low (0.04%). For this element the level of alkalinity in the leachate served to suppress cadmium mobility. The sand columns, with pH=10, leached only $7 \times 10^{-4}\%$ of the total cadmium in the waste. The MSW columns with 30% industrial waste loading, leached $6 \times 10^{-2}\%$, while the MSW columns with the same mass of industrial waste leached 1.2% of the total cadmium. The MSW columns with no industrial waste had the highest cadmium release rate with 1.3x the level of the MSW columns with 8% industrial waste. An interesting feature of the cadmium release from the MSW columns with industrial waste is that the rate of release has been increasing during the past year. This is at a time when BOD and pH have been stable.

ZINC

The industrial waste contains substantial levels of zinc (14%). The alkalinity of the leachate of the waste from the sand column resulted in only $4.3 \times 10^{-3}\%$ of the zinc from leaching from the column during the 5 year period. Interpreting the contribution to zinc leached from the MSW with the same mass of industrial waste is complicated by the high level of zinc from the MSW alone. The average amount of zinc leached from each MSW column was 3.63g per column. The mass leached from the industrial waste in sand was 0.019g per column. The same mass of industrial waste in MSW resulted in 0.47g of zinc being leached. Higher levels were found from columns with

30% industrial waste loading (1.92g) though still not at level found in the MSW columns.

OTHER ELEMENTS (Cu, Mn, Ca, Cr, Fe, Co)

The concentration of these elements in the industrial waste are shown in the Table. The addition of the industrial waste to MSW did not increase the concentration of the element in the leachate. The release of these elements from columns with the MSW was equal to or greater than from the columns with the additional 8% industrial waste. The columns having the alkaline solid waste generally showed much cleaner leachate (lower COD) and lower percentage of metals released. The low levels of metals released from the sand columns is a consequence of the low solubility of these elements in the alkaline leachate.

There is a good evidence that MSW has the capacity to inhibit the release of some metal values from wastes. This capacity is very beneficial in reducing the impact of the waste on the environment. This absorption capacity has been reported for a number of codisposal tests but the mechanism of metal retention suggested (either adsorption or precipitation) has not been proven. A more interesting possibility shown by the current research is that the presence of an alkaline waste can have a significant influence on the MSW leachate behaviour. The evidence from the study indicates that there is a reduced biological activity in the columns with industrial waste and this is supported by smaller values of total COD from the codisposal columns. Despite the low level of biological activity and low values of metals leaching from the columns, there is no direct evidence that the wastes have been stabilized. Most of the metal values remain in the MSW and have not been leached. The remobilization of cadmium after two years of low activity has not been explained.

In the next phase of the research we have proposed to investigate the chemical changes induced in the industrial waste in the MSW environment and to determine the extent of metal ion mobility in the MSW.

ACKNOWLEDGEMENTS

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TABLE
ANALYSIS OF THE INDUSTRIAL SOLID WASTE¹

Element	Fe	Zn	Ca	Mn	Pb	Cr	Cu	Cd
Total Mass(g)	851	441	388	128	61.7	6.57	5.63	1.02
Weight Percent	27.2	14.1	12.4	4.1	2.0	0.21	0.18	0.030
Leachate Analysis for Industrial Waste in Sand								
Mass Leached(g)	0.023	0.019	69.2	1.46	3.53	0.068	0.0135	0.0007
% Leached	2.7×10^{-3}	4.3×10^{-4}	17.8	1.1	5.7	1.0	0.24	7×10^{-4}
Leachate Analysis for Industrial Waste in MSW								
Mass Leached(g)	17.2	0.468	72.5	0.79	0.021	0.013	0.016	0.0126
% Leached	2.02	0.106	18.7	0.62	0.034	0.20	2.8	1.2
Leachate Analysis for MSW								
Mass Leached(g)	104.7	3.63	378.9	3.41	0.049	0.16	0.050	0.0169

The mass of industrial waste used in each column was 3.13 kg. The values reported in the table are the averages from 4 test cells for each condition (MSW, MSW+8% industrial waste, sand + industrial waste).

¹ The principal chemical species are in simple and complex oxide forms which include iron spinels and silicates.

VOLUME II
SESSION D
ANALYTICAL METHODS RESEARCH
VERBAL PRESENTATIONS

COUPLING AN EXTERNAL SOURCE TO A FOURIER TRANSFORM ION CYCLOTRON RESONANCE SPECTROMETER TO IMPROVE ITS USE FOR ANALYTICAL PURPOSES. T.B. McMahon* and C.E.C.A. Hop, Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University Of Waterloo, Waterloo, Ontario N2L 3G1

These days magnetic sector and quadrupole mass spectrometers are of prime importance for analysis in environmental research. To date the Fourier transform ion cyclotron resonance (ICR) spectrometer has not been considered seriously in analytical laboratories. This can partly be ascribed to the ultra high vacuum necessary for analysis, rendering chemical ionization, fast atom bombardment and coupling with a gas chromatograph impossible.

To extend the analytical capability of our Spectrospin CMS 47 Fourier transform ion cyclotron resonance spectrometer, we have successfully mated it with an external ionization source. In the external source sample material can be ionized via fast atom bombardment and chemical ionization. (Coupling with a gas chromatograph is possible as well, but it has not yet been installed.) Differential pumping ensures that the ICR cell is still at very low pressure ($< 5 \times 10^{-9}$ mbar). This instrument is thus ideally suited for the analysis of a wide variety of materials and offers the advantage over magnetic sector and quadrupole mass spectrometers that (i) the ionized material can be detected with superior mass resolution ($m/\Delta m > 1 \times 10^6$ at m/z 115) and (ii) MSⁿ experiments are possible without hardware changes. In addition, ion-molecule reactions of the ions externally generated can be studied in the ICR cell, which will lead to a better understanding of the processes taking place in chemical ionization.

We have used this technique to study a wide variety of organic pollutants, in particular phenols and polyhalogenated compounds. Chemical ionization is the preferred route for ionization. Collision induced dissociation and ion-molecule reactions of these ions leads to a better understanding of the chemical ionization process. Higher mass bio-organic and organometallic can successfully be analyzed with fast atom bombardment. Admission of ambient air to the high pressure source allows analysis of air containing volatile pollutants as well.

Thus, a Fourier transform ion cyclotron resonance mass spectrometer with an external source combines high pressure ionization techniques (for involatile, higher mass sample material) with high mass resolution detection.

THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN ENVIRONMENTAL SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY.

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INTRODUCTION

N-nitrosodimethylamine (NDMA) is a potent carcinogen found in tobacco smoke, food and beverages, industrial processes, water treatment processes and in the biosphere. The identification of NDMA in drinking water samples resulted in the need for an accurate determination of NDMA in various aqueous samples at the low part per trillion (ppt) level. NDMA is very soluble in water and is therefore difficult to extract. Also, its polarity makes it difficult to chromatograph on standard non-polar phase columns. The presence of chemical interferences causes difficulties in the identification and quantitation of NDMA because of the common low mass ions that are monitored. These difficulties require that a method for NDMA be selective and sensitive. The advantages and disadvantages of the various GC/MS techniques are discussed.

EXPERIMENTAL SECTION

Extraction Procedure:

Particulates in the sample were removed by filtering the sample through pre-extracted glass wool. The internal standard, d_6 -NDMA, was added to the sample and the sample mixed thoroughly. The pH of the sample was adjusted to 10-12 by addition of a sodium hydroxide solution. The sample was serially extracted three times with dichloromethane. The combined dichloromethane extract was washed with a dilute sulphuric acid (pH 2) solution and then filtered through anhydrous sodium sulphate. The extract was concentrated to 200 μ L.

Low Resolution Mass Spectrometry (LRMS):

Full scan GC/MS work was done on a Finnigan 4500. The mass range scanned was m/z 35-510 in 0.80 seconds. GC analysis was performed on a DB-5 (60m x 0.32mm i.d.) column.

Selected ion monitoring (SIM) studies were performed on an HP-5970 MSD. The ions monitored for NDMA were m/z 74 and m/z 42 with dwell times of 150 ms and 50 ms, respectively. Ions monitored for d_6 -NDMA were m/z 80 and m/z 46, with dwell times of 150 ms and 50 ms, respectively. A DB-1701 (30m x 0.25mm i.d.) column was used for the GC analysis. Additional SIM work was performed on the VG ZAB-2F at 1000 Resolving Power (RP).

High Resolution Mass Spectrometry (HRMS):

The VG ZAB-2F, a double focusing reverse geometry magnetic sector mass spectrometer, was tuned to 7000 RP for the high resolution work. A lockmass (m/z 68.9952, PFTBA) and the exact masses of NDMA (m/z 74.0480) and d_6 -NDMA (m/z 80.0857) were monitored. Dwell times were 100 ms for m/z 74.0480 and 50 ms for m/z 68.9952 and m/z 80.0857.

Quantitation of NDMA was accomplished by standard isotope dilution.

RESULTS AND DISCUSSION

NDMA does not chromatograph well on a DB-5 column. Alternate phases that gave better chromatography and sensitivity were DB-17 and DB-1701. However, there were still problems with co-elution of interferences.

A single quadrupole mass spectrometer in the full scan mode does not have the sensitivity to detect low ppt levels of NDMA in drinking water. However, it offers a degree of selectivity because interferences can be monitored in the mass spectrum. The instrument detection limit was 10 ng injected on a DB-5 column routinely used for characterization of extractable organics. The method detection limit for full scan GC/MS was 2 μ g/L.

The mass spectrum of NDMA consists of a molecular (quantitation) ion at m/z 74 (base peak) and an intense fragment (qualifying) ion at m/z 42. In the SIM mode, using a single quadrupole mass spectrometer, sensitivity has been increased over full scan MS but some selectivity is lost due to the presence of co-eluting interferences with the same nominal masses, m/z 42, 74, 46 and 80. This limits the usefulness of a single quadrupole mass spectrometer for the determination of NDMA, as co-eluting interferences could give erroneous results. The instrument detection limit was 20 pg injected. The method detection limit was 25-50 ng/L. The linear dynamic range was from 20 pg to 15 ng.

The VG ZAB-2F at low resolution (1000 RP) in the SIM mode is more sensitive than a quadrupole mass spectrometer in SIM mode for the quantitation ion (m/z 74) (200 fg injected). However, due to the voltage switching technique m/z 42 is weak relative to m/z 74.

In order to detect low ppt levels of NDMA confidently, the effects of chemical interferences co-eluting with the NDMA must be eliminated. Methyl esters are a common compound class that give rise to ions at m/z 74. To differentiate them from the NDMA, the VG ZAB-2F was run > 7000 RP. NDMA samples run at > 7000 RP in the single ion monitoring mode had excellent sensitivity and selectivity. This permitted the low ppt detection of NDMA with an instrument detection limit of < 1 pg. Procedure blanks showed a 1-4 ng/L level of NDMA and therefore the method has a detection limit set at 5-10 ng/L. The linear dynamic range for these parameters was 2 pg to 40 ng.

CONCLUSION

Of the techniques evaluated, single ion monitoring at > 7000 resolution is the method of choice because of its superior sensitivity, selectivity and linear dynamic range. This allows the determination of NDMA in environmental samples to be at the low ppt level.

REFERENCES

- Anal. Chem. (1982) 54, 1947.
- Anal. Chem. (1986) 58, 2919.
- J. Bull. Environ. Contam. Toxicol. (1980) 25, 106.
- J. Chromatogr. (1972) 64, 201.
- J. Chromatogr. (1973) 79, 57.
- J. Chromatogr. (1975) 109, 26.
- Tetrahedron Lett. (1970) 10, 737.

REAL TIME MEASUREMENTS OF DIMETHYLNITROSAMINE IN AMBIENT AIR BY MOBILE TANDEM MASS SPECTROMETRY

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ABSTRACT

Analysis of trace quantities of air toxics is becoming increasingly important in air pollution research. Dimethylnitrosamine (DMNA), $O=N-N-(CH_3)_2$, is a potent carcinogen reportedly found in tobacco smoke, cured meats and in some industrial processes involving the interaction of nitrite and dimethylamine. The real time detection of ppt levels of DMNA requires reliable sampling and calibration techniques, as well as, sophisticated analytical instrumentation. A method for DMNA detection was developed for mobile air monitoring applications using an atmospheric pressure chemical ionization (APCI) triple quadrupole (Q1, Q2, Q3) mass spectrometer (TAGA 6000). To calibrate the TAGA, a heated nebulizer was developed for injecting aqueous standards directly into the air sampling inlet of the analyzer. The nebulizer which consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for purge and carrier gases provides for the addition of controlled amounts of DMNA into the ion source. The ion chemistry of DMNA under ammonia APCI conditions is relatively simple: DMNA molecules undergo proton transfer reactions with ammonium ions (NH_4^+) to yield parent ions at 75 amu (atomic mass units). Parent ions, selected in the first quadrupole (Q1), undergo collisional activated dissociation (CAD) with argon in Q2 (RF only). The resultant daughter ions at 15, 43 and 58 amu are identified by Q3. Multiple reaction monitoring (MRM) of the parent/daughter ion pairs 75/15, 75/43 and 75/58 is used to monitor DMNA in real time. The response of the TAGA system to DMNA was characterized through six-point calibration curves, in the concentration range of 0 to 80 ng/m³. Low detection limits and reproducible calibration data were accomplished by the optimization of various MS/MS and nebulizer parameters. This unique method was recently applied to an air monitoring study in Ontario where DMNA was measured and tracked to its source using the mobile TAGA 6000. The real time limits of detection for DMNA were better than 5 ng/m³ (2 ppt) during a two-week field survey.

INTRODUCTION

Real time detection and quantification of air contaminants at trace levels require sensitive instrumentation and advanced calibration techniques. Recently there was a need for the development of a method to detect dimethylnitrosamine (DMNA), $O=N-N-(CH_3)_2$, with high specificity supported by accurate calibrations. In 1989, a preliminary study conducted using the Ministry's TAGA 3000, a single quadrupole mass spectrometer (MS), showed that DMNA can be detected at levels as low as 15 ng/m³ in real time. Depending on the ionization technique and the complexity of the sample matrix, identification of contaminants with single MS systems may be tentative. Thus, detailed research on DMNA method of detection was performed with the Ministry's mobile TAGA 6000 triple quadrupole mass spectrometer. Owing to the superior analytical capabilities of tandem mass spectrometry, difficulties of contaminant identification are greatly reduced while maintaining real time detection. The mobile TAGA 6000 has been used for on-site analysis of numerous contaminants from a variety of industrial sources in Ontario, and during environmental emergencies such as the Hagersville tire fire in February 1990. The successful application of the TAGA 6000 depends primarily on well established quality

assessment/quality control (QA/QC) programs and optimum instrumentation performance. For this study it was necessary to develop and evaluate the performance of a heated nebulizer for injecting controlled amounts of DMNA liquid standards into the TAGA ion source. The standard injection technique was used for calibration purposes and for establishing the real time limits of detection for DMNA. This novel method was recently applied to an air monitoring survey in which trace levels of DMNA were measured.

EXPERIMENTAL

A schematic diagram of the TAGA 6000 is shown in Figure 1. The basic operation is governed by the principles of tandem APCI mass spectrometry. Parent ions, formed in the APCI region, pass through an orifice into the vacuum chamber where they are separated by the first quadrupole and fragmented with argon gas in the second quadrupole (RF only). The resultant fragments, or daughter ions, are analyzed by the third quadrupole. Compound identification is achieved by comparison of the daughter ion spectra to a standard CAD (collisionally activated dissociation) library spectra. Compound quantification is accomplished by calibrating the response of the TAGA to known amounts of the calibrant admitted into the inlet air flow.

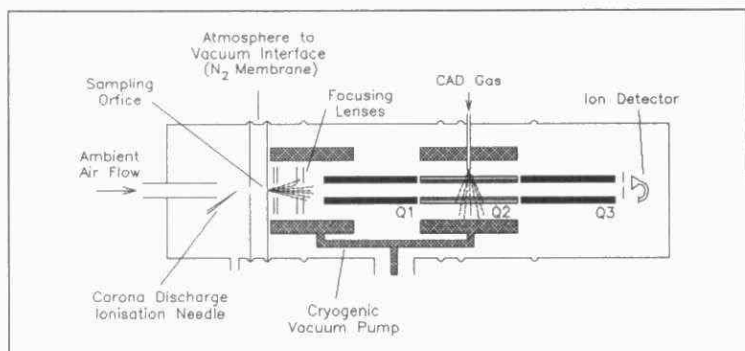


Figure 1: Schematic diagram of the TAGA 6000 mass spectrometer.

Optimization of ion signals and calibration of the TAGA sensitivity were achieved by introducing known amounts of DMNA-water solution into the ion source. DMNA photo-degrades upon exposure to sunlight; consequently, DMNA standards were wrapped in aluminum foil and stored in a cool, dark area. Calibrations were performed under minimum exposure to light.

The DMNA aqueous standard (8.04 ng/L) was introduced into the inlet air flow via a heated nebulizer developed by the Mobile Monitoring Group. A schematic diagram of the nebulizer is shown in Figure 2. The nebulizer consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for nebulizing and purging gases; this configuration ensures uniform sample atomization thus providing for the addition of controlled amounts of DMNA into the TAGA ion source. The calibrant was injected into the nebulizer with a 0.5 mL, 22s gauge Hamilton Gastight syringe mounted in a Harvard (model 22) syringe infusion pump. The flow rates of DMNA into the TAGA ion source were controlled by the speed of the pump. Flow rates 0 to 0.9 $\mu\text{L}/\text{min}$ allowed a DMNA concentration range of 0 to 80 ng/m³ to be generated in the APCI source. Higher flow rates were also used to examine the linearity of the response curves at concentrations up to 4000 ng/m³.

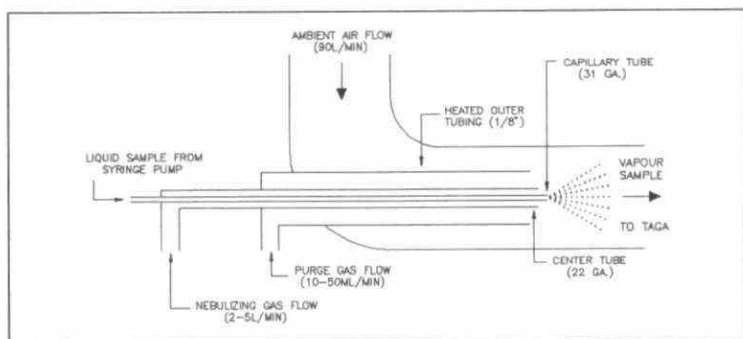


Figure 2: Schematic diagram of the heated nebulizer.

The parent ion at 75 amu, protonated DMNA, and the major daughter ion at 43 amu were optimized by varying MS/MS parameters. A low potential between the sampling orifice and an adjacent ion transfer lens (cluster breaker) was required to minimize the degree of fragmentation in the ion source. The corona discharge needle axial position was set approximately 1 cm from the sampling orifice. The chemical noise at 75 amu was sensitive to the radial position of the discharge needle; best results were obtained with the tip of the discharge needle slightly off center (ca. 0.5 mm) with respect to the sampling orifice.

The temperature of the inlet air was maintained at 50 °C in order to maximize ion signals and minimize memory effects. Several temperature settings were used for the nebulizer; in terms of DMNA signal stability, satisfactory results were obtained by operating the nebulizer in the range of 30 to 50 °C.

RESULTS AND DISCUSSION

The response of the TAGA to DMNA and the chemical background were examined under water and ammonia CI conditions. Owing to the higher proton affinity of NH_3 as compared to that of H_2O , ammonia CI simplifies the mass spectra of complex air samples. Ammonia CI suppressed the background (viz. chemical noise) by at least a factor of 10 over H_2O CI, allowing for lower detection limits. The chemical noise under ammonia CI conditions was only 1 to 2 ion counts per second (ICPS) for the three parent/daughter ions of DMNA.

The ion chemistry of DMNA gas under TAGA/APCI conditions is relatively simple: DMNA molecules undergo proton transfer reactions with hydronium ions (H_3O^+) or ammonium ions (NH_4^+) to yield parent ions at 75 amu (atomic mass units). Fragmentation of protonated DMNA in the APCI source was found to be negligible. Under collisionally activated dissociation (CAD) daughter ions at 43, 15 and 58 amu were observed. The possibility of DMNA produced in the ion source from dimethylamine (DMA) and oxides of nitrogen was ruled out; when 200 ppb of DMA and 1% NO was admitted into the TAGA source, DMNA was not observed.

An MS/MS library ion mass spectrum for DMNA was created using 50 eV ion energy and argon CAD gas thickness of 300×10^{12} molecules/cm². The CAD fragmentation pattern, shown in Figure 3 (bottom), is dominated by three daughter ions at 15, 43 and 58 amu. Figure 3 (top) shows daughter ion spectra for $m/z=75$ amu obtained downwind of a chemical plant. The CAD spectra of the "unknown" is compared

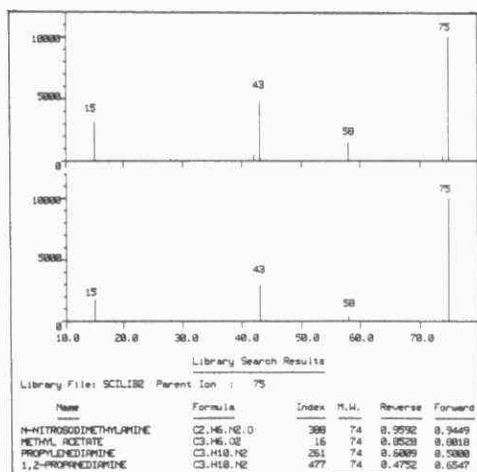


Figure 3: The CAD spectra for the mass 75 parent ions obtained downwind of a chemical plant (top) and CAD library mass spectrum of DMNA (bottom).

with standard CAD library spectra; agreement between the "reverse" and "forward" library search results and their closeness to unity, indicate the degree of certainty for compound identification. The "best" search results were obtained for DMNA. A closer examination of the CAD spectra of the second listing showed that methyl acetate lacks the 58 amu fragment.

Six-point calibrations of DMNA were performed by simultaneously recording the responses of three parent/daughter (P/D) ion pairs. An example of a calibration, in the concentration range 0 to 80 ng/m³ is shown in Figure 4; these data were obtained under ammonia CI conditions. The slopes of the response curves are measures of the sensitivity of the APCI MS/MS system to DMNA. To avoid system contamination, the saturation point for response non-linearity was not determined; however, linear response was observed up to 4000 ng/m³ DMNA.

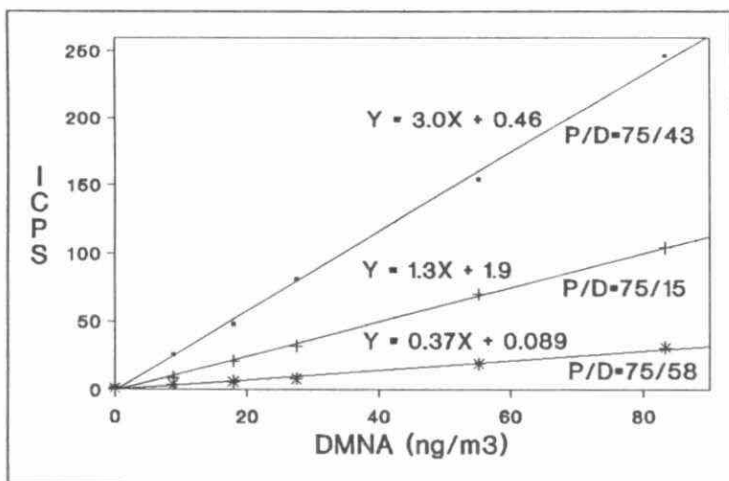


Figure 4: Example of a DMNA calibration (TAGA 6000).

Figure 5 shows the detection limits (DL) for DMNA, based on the average of the DL values of the three parent/daughter ions. Detection limits are defined as 3 times the standard deviation of the background signals divided by the sensitivity, or the slope of the response curve. Detection limits in ambient air were determined at various locations in

selected cities in southern Ontario over a period of several days. The variation in DL values from day to day is readily apparent: the DL's ranged from 2.9 to 4.8 ng/m^3 with a mean value of 3.8 ng/m^3 and a standard deviation of 0.67 ng/m^3 .

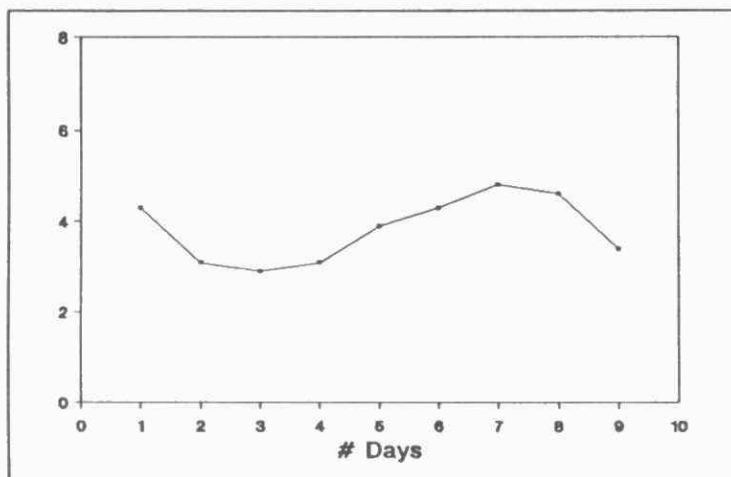


Figure 5: Detection limits of DMNA in ng/m^3 .

The detection limits are affected most by the ambient air matrix, the measurement dwell time and the position of the corona discharge needle relative to the sampling orifice. For instance, slight changes in the radial position of the discharge needle can alter signal stability and, subsequently change detection limits. Also, longer measurement dwell times produce lower detection limits; for example, a dwell time of 1 second results in a detection limit of 3 ng/m^3 whereas a dwell time of 0.1 seconds yields a DL of 30 ng/m^3 .

This method was field-tested in the spring of 1990 by conducting an air monitoring survey of DMNA in the vicinity of a suspected source. During the two-week survey, DMNA detection limits were determined at least twice daily; on average, the DLs were better than 5 ng/m^3 . Ambient DMNA levels were recorded at several locations both upwind and downwind of the source. Figure 6 (a) shows the real time measurements of DMNA recorded every 5 seconds for a period of 30 minutes at a fixed location downwind of the source. Rapid changes in DMNA levels were mainly due to variations in the wind

direction. The downwind response profiles of the parent/daughter ion pairs are similar indicating the presence of DMNA. In contrast, data obtained upwind, Figure 6 (b), show that changes the parent/daughter ion profiles do not correlate, indicating the absence of DMNA.

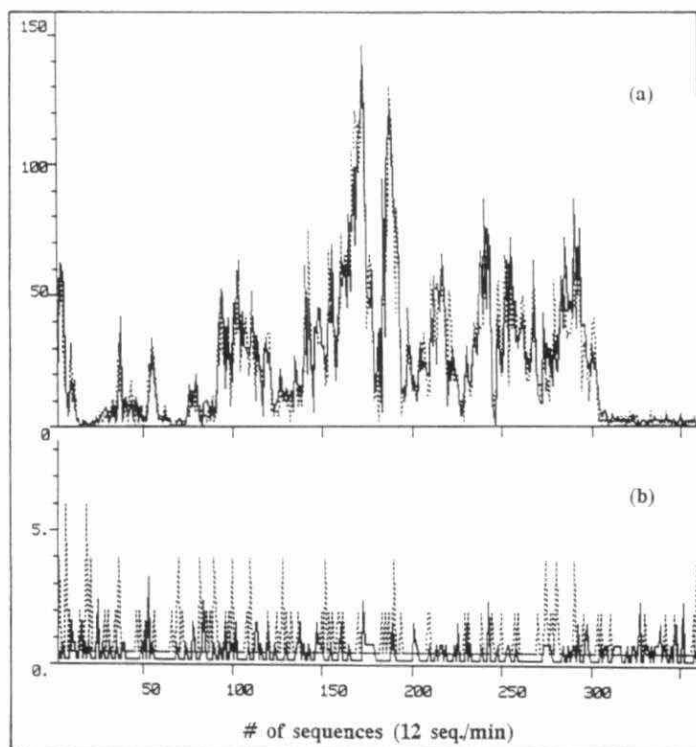


Figure 6: Real time monitoring of DMNA downwind of a chemical plant (a) and background levels of ion pairs 75/15, 75/43 (b). Y-axis are in ng/m^3 .

Dimethylnitrosamine was also measured while the mobile TAGA criss-crossed the streets downwind of the plant. Figure 7a shows an example of plume tracking data; the concentration of DMNA varied with distance from the source: 51 ng/m^3 were recorded.

at 300 m and 21 ng/m³ at 600 m. At distances greater than 1 km, DMNA was not detected. Figure 7b shows the real time data as recorded by the TAGA while transecting the plume at various distances from the source.

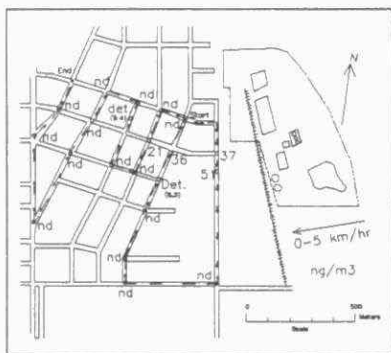


Figure 7a: Plume tracking for DMNA downwind of a chemical plant.

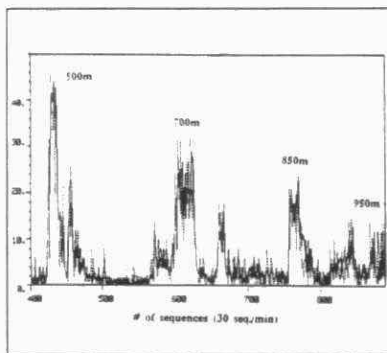


Figure 7b: Plume tracking concentration profile of DMNA in ng/m³.

SUMMARY

The Mobile Monitoring Group of the Air Resources Branch developed a new method to monitor, in real time, trace amounts of atmospheric DMNA based on the Ministry's mobile TAGA 6000, an APCI/MS/MS system. Several results were obtained from this study. Ammonia is the preferred CI reagent for monitoring DMNA in ambient air, since it reduces the number of interferences through selective ionization. Compared with water CI, ammonia CI gave considerably lower background levels, improving specificity and lowering detection limits. A calibration procedure for injecting aqueous DMNA standards through a heated nebulizer which was developed, proved to be reliable and reproducible at final gas phase concentrations up to 80 ng/m³. The *real time* limits of detection of DMNA in ambient air was of the order of 5 ng/m³ or 2 ppt. This unique technique was applied to measuring ambient DMNA levels in Ontario.

THE ANALYSIS OF SMITHVILLE DRINKING WATER FOR PCBs

D.A.Sutherland * , J.Waugh, L.Paul, A.Rayner, G.Reuel

The remediation of a waste storage site contaminated with polychlorinated biphenyls (PCBs) near Smithville Ontario is a high priority and high profile project. The importance of protecting public drinking waters and the inherent high costs of remediation underscore the need for comprehensive QA/QC, confidence in the analytical result and a turnaround time for analytical results that allows for responsive action. After considerable Research and Development funded by CANVIRO Laboratories, and method performance testing by the Ministry of the Environment (MOE), CANVIRO Laboratories was awarded a multi-year contract to analyze groundwater for PCBs and report these results immediately to the Ministry.

Traditionally the detection of PCB's has relied on the electron capture detector (ECD). Any contentious samples identified using this technique were often sent to a mass spectrometry department in hopes that a confirmatory analysis could be made. Often the sensitivity of the GC/MS was insufficient.

To reduce the time and costs in obtaining results for this project, CANVIRO Laboratories developed a method to analyze PCB's in waters at the required low limits of detection directly by GC/MS on a routine basis, thus providing simultaneous low level detection and positive confirmation.

MOE DETECTION REQUIREMENTS vs CANVIRO PERFORMANCE (ppb)

	MOE "w"	CANVIRO "w"
1,2,4-TCB	0.005	0.002
1,2,3-TCB	0.005	0.002
Arochlor 1242	0.020	0.005
Arochlor 1254	0.020	0.010
Arochlor 1260	0.020	0.010

TCB - Trichlorobenzene
w - range 0.5-1.0 standard
deviations from low level
replicate analyses

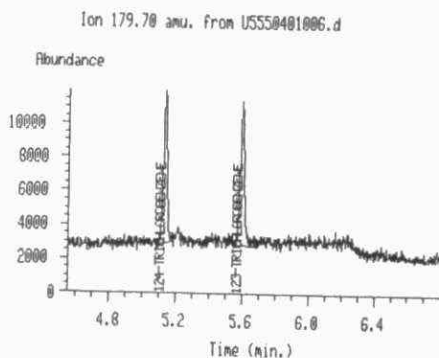
The analysis by GC/MS is relatively free from the influence of co-eluting pesticides and phthalates that can and do interfere when using an ECD detector. The absence of any clean-up steps in CANVIRO's procedure and the reasonable concentration factors (ie., 800 mL sample to a final 1 mL extract) provide excellent method precision. The operating conditions of the GC/MS and typical demonstrations of method sensitivity are presented below.

Instrumental Parameters:

HP - MSD System:
5890 - Gas Chromatograph
5970B - Mass Selective Detector
7673A - Robotic Autosampler
Carrier Gas : Helium
Temp Program : 90°C for 0.4 min,
Ramped @15°C/min to 130°C
Ramped @ 5°C/min to 270°C
Ramped @20°C/min to 315°C
Final Hold 1 min
Injector Temp : 280°C
Interface Temp: 290°C
Splitless Time: 0.4 min
Column: RTX-5, 60 metre x 0.25 mm ID
x 0.25 phase thickness

Demonstrated Sensitivity

6 Picograms Injected of
1,2,4 and 1,2,3-Trichlorobenzenes



Sample Extractions:

A liquid-liquid extraction is carried out using a magnetic stir plate and teflon stir bar. Each 800 mL sample is extracted with 60 mL of methylene chloride, in the original sample bottle after the addition of a teflon stir bar. After 20 minutes of vigorous mixing, a separatory funnel is used to separate the solvent and aqueous phases. The aqueous phase is extracted in the sample bottle with two more 60 mL methylene chloride aliquots.

The extracts are dried with anhydrous sodium sulphate and concentrated to a volume of 1 mL via rotary evaporation. No clean-up or fractionation methods are required due mostly to the specificity of GC/MS.

Identification and Quantification:

The GC/MS in the Selected Ion Monitoring (SIM) mode is very specific. Selected ion groupings effectively make the GC/MS into a cogener specific detector.

Many excellent publications have shown identification strategies that include multiple regression, least squares analysis or pattern recognition software. CANVIRO Laboratories modified MOE's Webb and McCall method and have developed the following rules that are more easily integrated into a routine that approaches such as the SIMCA pattern recognition program.

- i) The sample must show a specific pattern similar to an Arochlor or mixture of Arochlors,
 - ii) An externally run standard of a 1:1:1 mixture of Arochlors 1242:1254:1260 is used for quantification. This calibration standard is at a concentration of approximately 100 ng/mL per Arochlor,
 - iii) Eight of the most significant peaks are chosen from each of the Arochlors (Total 24 peaks),
 - iv) A minimum of 4 of the 8 peaks must be present to confirm the presence of an Arochlor,
 - v) A minimum of 3 of these peaks are averaged and are used for quantification,
 - vi) If any sample peaks are proportionately greater in peak height than what appears in the 1:1:1 mixture, the sample peak is not used for quantification,
 - vii) Total PCB's is reported as the summation of the concentrations reported for each Arochlor.
-

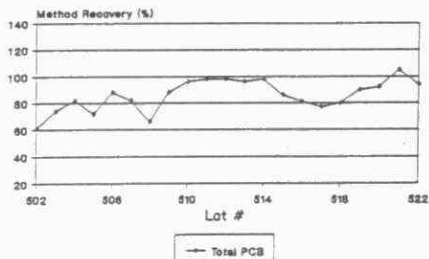
Quantitation is performed by an Internal Standard Method using a pre-injection spike of D10-Anthracene directly into the extract. All data entry to the Ministry of the Environment is made via modem into MOE's Laboratory Information System (LIS).

Quality Assurance / Quality Control:

Incorporated into the QA program is procedures to monitor and document:

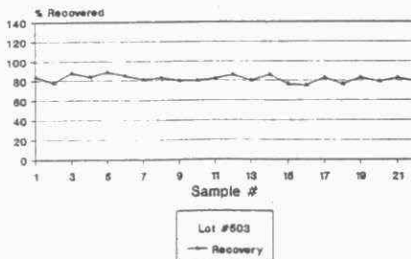
- 1) daily instrument sensitivity
- 2) laboratory method blanks
- 3) laboratory method spikes
- 4) percent recovery of the pre-extraction spike surrogate 2,4,6-Tribromobiphenyl for each extract
- 5) MOE blind spike acceptance program for any new extraction personnel

Method Spike History
Total Polychlorinated Biphenyls



Canviro Analytical Laboratories Ltd.

Surrogate Recoveries
Week 13



Surrogate: 2,4,6-Tribromobiphenyl

CANVIRO Analytical Laboratories Ltd.

CANVIRO Analytical Laboratories Ltd.

In conclusion the confidence in analytical data is becoming evermore important. GC/MS has proven to be a sensitive, selective, highly reliable and highly rugged method of analysis.

Many thanks to Dr. David Hall and his staff of the Drinking Waters Section at the Ministry of the Environment's Rexdale Laboratories.

Evaluation of Environmental Sources of Polychlorinated Biphenyls using Chemometric Methods.

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A number of chemometric techniques were applied to the interpretation of congener-specific high-resolution gas chromatography analyses of polychlorinated biphenyls (PCBs). The numerical techniques employed included SIMCA 3X pattern recognition, principal components analysis, and KNN (K-nearest neighbor statistical analysis). The objectives of the study were to identify, classify, and categorize environmental PCB samples. It was found that the quantitative compositions of commercial Aroclor PCB congeners allow for identification of Aroclor mixtures (such as Aroclors 1221, 1232, 1242 etc.) in environmental samples. Knowledge of the Aroclor composition of water, sediment, and biota samples facilitates assessment of environmental origins and environmental degradation patterns.

Introduction

This paper presents several numerical techniques which allow for the tracing of environmental sources of PCBs, and interpretation of how PCB profiles are altered as a result of introduction into the ecosystem. All of the PCBs that were produced in North America came from a single manufacturer, the Monsanto Chemical Company in the United States. The various technical mixtures provided to industry by this company were given the trade name Aroclor, and were designated according to the chlorine content in the biphenyl molecule. This chlorine content varied from 21% to 68% chlorine by weight. The PCB mixtures produced by this company consist of only a relatively small number of specific grades of Aroclors. These included Aroclors 1221, 1232 1016, 1242, 1248, 1254, 1260, 1262, and 1268, where the last two digits indicate the percentage of chlorine. These commercial products were analyzed by the manufacturer, and variations in the chlorine content were usually adjusted with higher or lower chlorinated products to obtain an average value as specified for a particular Aroclor. Consequently, variations in PCB isomers were significant between batches. However, congener group variations were less pronounced.

Experimental

Sediment, water, and biota samples were collected from Wheatley and Hamilton harbours. Sediment samples were collected by Eckman dredge, water samples were collected by a Van Dorn water bottle. Physa integra (snail), Zonitoides arborens, Lymnaea stagnalis (snail), pumpkinseed sunfish (Eupomotis gibbosus) (Lepomis?), and Isopods were collected from the nearshore and offshore areas.

Open tubular column gas chromatography analyses were performed on the water, sediment, and biota samples. A Varian Model 6000 GC equipped with a cold on-column injector and an electron-capture detector were utilized. Peaks were identified by a method of relative retention time matching. Decachlorobiphenyl was used as a reference peak. Relative retention time values for the PCB congeners were calculated as the ratio of the individual peak retention time to that of decachlorobiphenyl. The samples were quantified using calibrated Aroclor standards in a 1:1 mixture.

Interpretation of results

Typical chromatograms of commercial Aroclors are given in the figure 1. These chromatograms are the result of the analysis of Aroclor standards obtained in ampoule form from the US-EPA in Cincinnati, Ohio. The various congener groups are indicated by integer numbers on the chromatograms. There is a very noticeable change in the proportion of the PCB congener groups from lower to higher chlorinated Aroclors. It readily becomes apparent that visual inspection of isomer or even congener group patterns from sample chromatograms is extremely tiresome and prone to errors when the objective is to evaluate which Aroclor mixture is present in an environmental sample. This is greatly complicated by the two facts : (1) Many industrial applications of PCBs involved two or more mixtures of Aroclors; and (2) The introduction of PCBs into the environment results in some modification of the isomer and congener group patterns due to various physical, chemical, and biological fractionation mechanisms.

If the composition of the chlorine content of the Aroclors were represented as percentages of the various congener groups, such as in table 1, the evaluation of PCB profiles would be considerable simplified. This manner of presentation is also convenient for input into many numerical or statistical programs. Some industrial PCB applications are actually mixtures of two or more Aroclors. Industrial mixtures may include binary mixtures composed of two Aroclors, ternary mixtures composed of three Aroclors, and even quaternary mixtures composed of four different Aroclors. Such theoretical industrial PCB mixtures can be numerically approximated by manipulation of the Aroclor end- members (Onuska et. al., 1985).

The results from the analysis of PCBs in the water samples (table 2) from the two harbours revealed that the more chlorinated PCB congeners were present in higher proportions in Hamilton Harbour. Total PCB concentrations were approximately the same for both harbours. However, all water samples contained levels of PCB over the MOE objective for the protection of aquatic habitats which is 1 ug/L.

The sediment results (table 3) exhibit more pronounced variations in the PCB loadings for the two harbours. Once again the more chlorinated congeners are more prevalent in the Hamilton Harbour samples. However, the PCB concentration in the Hamilton Harbour sediment ranged to approximately 10 times that of Wheatley Harbour. The PCB levels in the sediment samples were alarmingly high, especially station 3 in Hamilton Harbour which displayed 14.2 mg/Kg of total PCB.

Concentration patterns of PCB congeners were similar in all types of biota for the two harbours (table 4) with the exception of the Oligochaete worms. This is possibly due to the heterogeneous nature of the offshore area of Hamilton Harbour (with respect to the nearshore area) from which the oligochaete worms were sampled. Whereas the smaller Wheatley Harbour is more homogeneous.

A supervised learning technique was applied to both the theoretical Aroclor mixtures discussed above, and the actual environmental sample results. In the supervised learning approach advance knowledge of sample category or membership is used to train a computer program as to how best to classify unknown samples. Three principal components were extracted from a dataset containing either the Wheatley or Hamilton Harbour data plus the EPA Aroclor standards.

Hamilton Harbour

A plot of the first two components for Hamilton Harbour reveals that the sediment and biota samples appear to plot together in a bunch delineated by Aroclors 1254, 1260, 1262, and 1248. A somewhat separate group includes the two water samples. It is interesting to note that the water sample obtained from the middle of the water column plots near the Aroclor 1248 point; whereas the water sample obtained from the water collected near the bottom plots closer to the sediment and biota samples. Due to the low solubility of PCBs in water, it is possible that the PCB congener profiles observed in the water samples are somewhat depleted with respect to the more highly chlorinated groups, alternately one could assess the water PCB profile as representing the least degraded or modified PCB samples, and as such, more representative of the original source of PCB contamination Hamilton Harbour. If so, the sediment samples indicate that a fractionation mechanism may be responsible for modifying the PCB profile so that the more highly chlorinated congeners are preferentially retained within the sediment.

Wheatley Harbour

The plot of the Wheatley Harbour data is similar but not identical to the Hamilton Harbour data. As before, two groupings can be observed, one corresponding to water samples, the other containing the sediment and biota samples. However, the two water samples plot much closer together than they did in the Hamilton Harbour dataset. The sediment/biota samples also plot more closely together than they did in the Hamilton Harbour dataset. This could indicate that the PCBs present in Wheatley Harbour have less diverse origins than PCBs found in Hamilton Harbour. This seems likely as Hamilton Harbour has a diverse industrial base with several possible sources of PCBs. PCBs found within Hamilton Harbour could originate from various steel industry sources, incinerator emissions, and other industries,

whereas the only industry found at Wheatley Harbour is related to commercial fishing.

Once again the water samples plot closer to the lower chlorinated Aroclor groups, and the sediment/biota plot closer to more highly chlorinated groups. The sediment/biota sample plot closer to Aroclor 1254 than did the Hamilton Harbour samples. The sediment/biota samples also plot further away from the more chlorinated Aroclors 1260 and 1262 than was the case with the Hamilton Harbour samples.

Because of the limited amount of industry present in Wheatley Harbour, the possible sources of PCB contamination are rather limited. The major source of PCBs in Wheatley Harbour is likely to be PCBs which arose from paints applied to fishing boats. PCBs used to be added to paints as softening or plasticizing agents. It is known that the Aroclors added to paints were a mixture of 1248 and 1254. The conclusion that these paints are the source of environmental PCBs at Wheatley Harbour appears to be borne out by the principal components plot. All samples plot between limits derived by these two Aroclor groups, with little deviation towards the other Aroclors (which is unlike the Hamilton Harbour dataset). Only a small amount of partitioning between the higher/lower chlorinated Aroclors appears to have taken place in the Wheatley Harbour samples.

As mentioned previously, the industrial base of Hamilton Harbour precludes an easy assessment of PCB source material. It appears that four or five different Aroclors may be represented in the Hamilton Harbour dataset. These include Aroclors 1254, 1260, 1262, 1248, and possibly 1242. PCBs in transformer fluid are frequently mixtures of Aroclors 1242, 1254, and 1260. These mixtures often did not contain Aroclor 1248. It is possible that a mixture of these three Aroclor end members would produce points which plot near the observed data points (and also near Aroclor 1248). It is known that the steel industry used to coat steel products with PCBs during the finishing process. These PCBs often consisted of the less chlorinated Aroclor groups. These Aroclors ranged from Aroclor 1016 to Aroclor 1242. It would seem that either these PCBs were not introduced into the Harbour, or have since degraded to appear as the more highly chlorinated forms.

Summary

It was found that the quantitative compositions of commercial Aroclor homologue groups allow for quantification of binary, ternary, and quaternary Aroclor mixtures. Knowledge of the Aroclor technical mixture composition of environmental PCB samples facilitates assessment of environmental origins. Modifications to PCB profiles, as a result of environmental degradation, can also be evaluated using similar numerical techniques. These techniques have been applied to PCB samples obtained from sediment, water, and biota from Wheatley and Hamilton harbours.

REFERENCES

- 1 W.H.J. Strachan, H.Huneault, J. Great Lakes Res. 5, (1979) 61.
- 2 P.C. Bauman, D.M. Whittle, Aquatic Toxicol. 11,(1988) 241.
- 3 R.F. Frank, R.L. Thomas, M. Holdrinet, A.L.W. Kemp, H.E. Braun, J.-M. Jaquet, Sci.Total Environ. 8,(1977) 205.
- 4 R.F. Frank, R.L. Thomas, M. Holdrinet, A.L.W. Kemp, H.E. Braun, J. Great Lakes Res., 5, (1979) 18.
- 5 A. Mudroch, F.I. Onuska, L. Kalas, Chemosphere, 18,(1989) 2141.
- 6 F.I. Onuska, A. Mudroch and S. Davies, J.High Resoln.Chromatogr.&Chromatogr.Comm.,8,(1985) 747.
- 7 F.I. Onuska, K.A. Terry, J.High Resoln.Chromatogr.&Chromatogr. Commun.,9,(1986) 671.
- 8 D.L. Massart, B.G.M. Vadegiuste, S.N. Deming, Y. Michotte, L. Kaufman, *Chemometrics: A Textbook*, Elsevier, Amsterdam,1988, p.339.
- 9 S. Word and M. Sjostrom, *Chemometrics: Theory and Applications* ed. B. Kowalski, ACS Symp.Ser.No.52, 1977, pp.243.
- 10 E.Jellum, I. Bjornson, R. Nesbakken, E. Johansson, S.Word, J. Chromatogr., 217,(1981) 231.
- 11 W.J. Dunn III., D.L. Stalling, R.T. Schwartz, J.W. Hogan, J.D. Petty, E. Johansson, S. Word, Anal.Chem. 56, (1984) 1308.
- 12 D.L. Stalling, T.R. Schwartz, W.J. Dunn III., S. Word, Anal.Chem., 59,(1987) 1853.

Table 1. Composition of Individual Homologue Groups in Selected Aroclors

AROCLOR	1248	1254	1260	1262
Monochloro-	0.0	0.0	0.0	0.0
dichloro-	1.0	0.0	0.3	0.4
trichloro-	28.3	0.3	0.6	1.0
tetrachloro-	54.6	15.0	0.7	0.7
pentachloro-	11.4	44.1	8.0	2.4
hexachloro-	2.6	35.1	42.0	25.5
heptachloro-	1.4	4.6	35.6	43.5
octachloro-	0.6	0.8	11.8	24.3
nonachloro-	0.1	0.1	0.9	2.2
decachlorobiphenyl	ND	ND	0.1	0.5

Table 2. Residues of PCBs in Water at Two Harbours (ng/L)

PCB-homologues	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Total
HAMILTON HARBOUR :							
Station 1	39.1	68.8	69.7	24.4	10.3	2.4	214.7
Station 2	26.3	33.3	18.8	5.0	1.6	1.0	86.0
WHEATLEY HARBOUR :							
Station 1	36.2	148.5	91.0	13.0	2.3	0.1	291.1
Station 2	13.9	35.9	27.3	7.4	1.8	0.1	86.4

Table 3. Distribution of PCBs in Sediments ($\mu\text{g/kg}$)

Homologue	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	Total
HAMILTON HARBOUR								
Station 1	97.4	134.9	324.6	284.5	30.9	70.9	5.3	948.5
Station 2	41.0	72.4	174.3	140.3	146.2	31.4	2.3	608.0
Station 3	733.0	1065.0	3321.0	3289.0	4044.0	985.0	748.0	14185.0
Station 4	235.7	451.0	777.5	451.3	462.7	112.0	8.8	2499.0
Station 5	205.9	441.6	724.8	443.6	350.5	75.8	6.1	2248.0
Station 6	148.4	267.4	825.6	744.2	865.1	206.3	15.8	3073.0
WHEATLEY HARBOUR								
Station A	28.8	111.2	474.0	358.0	175.8	26.6	2.4	1176.8
Station B	5.6	20.0	67.8	51.0	16.8	2.0	2.8	166.0
Station C	14.8	64.6	252.2	140.8	91.6	14.6	1.4	580.0
Station D	5.8	30.8	103.2	53.0	31.2	5.6	0.4	230.0
Station E	5.6	34.0	155.4	110.0	40.2	5.8	0.1	351.1
Station F	21.4	54.2	189.8	132.2	59.6	7.7	0.5	465.0

Table 4. Distribution of PCBs in Biota ($\mu\text{g/kg}$ wet weight)

Homologue Tri- Tetra- Penta- Hexa- Hepta- Octa- Total

HAMILTON HARBOUR

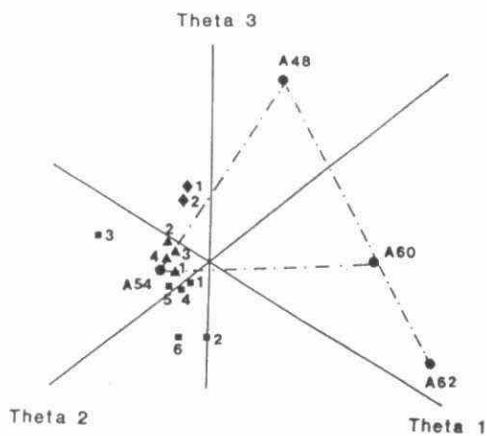
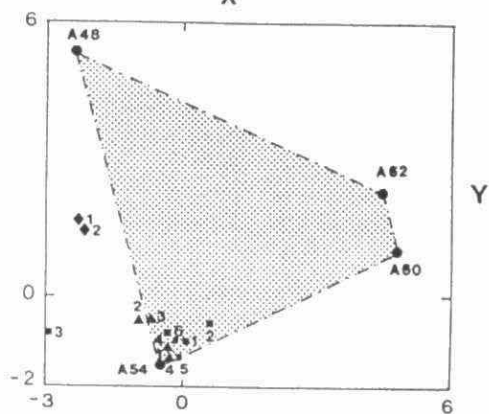
Isopoda	16.7	32.2	37.9	17.5	5.3	ND	109.6
<i>Physa integra</i>	5.5	36.5	71.2	32.0	12.0	1.1	158.3
Oligochaetes	32.6	39.5	54.5	45.3	30.5	4.8	207.2

WHEATLEY HARBOUR

Fish (*Eupomotis*

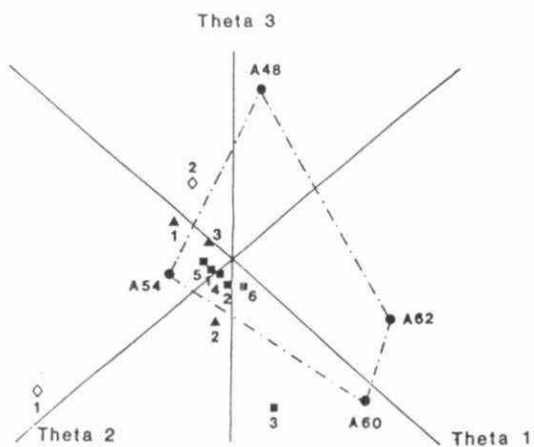
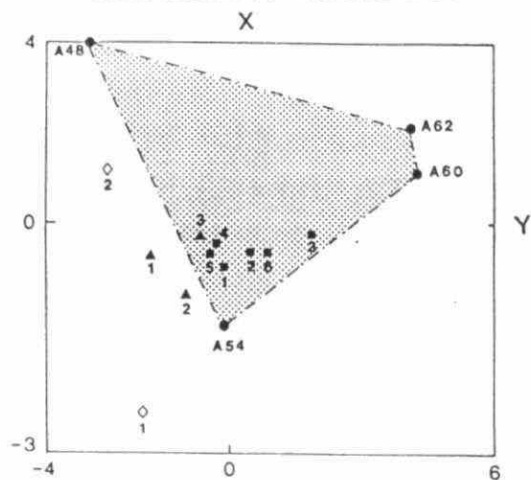
<i>gibbosus</i>)	7.0	10.3	26.5	21.6	3.9	ND	69.3
<i>Zonitoidus</i>	5.1	17.3	64.8	46.3	16.3	1.6	151.4
<i>arborens</i>							
<i>Physa integra</i>	5.6	14.3	27.9	21.2	3.1	ND	72.1
Oligochaetes	22.4	40.2	102.8	72.2	22.6	2.5	262.7
<i>Lymnea stagnal.</i>	1.2	7.4	22.7	24.5	2.9	ND	58.7

WHEATLEY HARBOUR



Water (◆), Sediment (■), and Biota (●)

HAMILTON HARBOUR



Water (◆), Sediment (■), and Biota (●)

ISOLATION AND DERIVATIZATION OF CHLORO-AROMATIC ORGANIC ACIDS
ON SOLID SUPPORT

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INTRODUCTION:

Gas chromatographic determination of the chlorophenoxy acetic acid (ClPAA's) herbicides and the breakdown products ie the chlorophenols (ClP's) from water requires that analytes first be isolated from matrix and then derivatized at the acidic functionalities. Reaction with pentafluorobenzyl bromide (PFBBR) (1) or methanolic BCl₃ (2), or silylation (3) with cyano containing reagents and with have been used to prepare the derivatives for gas chromatographic determination of parent herbicides and the corresponding phenols. Standard EPA procedures are based on derivatization with PFBBR but the process is complex and involves use of toxic catalysts such as crown ethers (1). The appropriate use of solid supported processes (4-6) could be used to simplify such procedures and eliminate the use of toxic materials in the analytical laboratory. Ideally these processes on solid supports should include both adsorption and derivatization.

We investigated the simultaneous adsorption and pentafluorobenzylation of ClPAA's and ClP's on solid supports directly from 5-20 ml of water in order to determine if this simplifying technology could be applied to environmental problems. Electrophoric and water insoluble pentafluorobenzyl (PFB) derivatives suitable for gas chromatography were via reaction with PFBBR supported on XAD-2 (7-12).

While simultaneous isolation/derivatization was facile there was also a simultaneous production of the PFB esters of fatty acids that are a common contaminant of glassware and all samples that have biological materials in them (e.g. cells, cellular debris). These interfered with determination of the analyte and resulted in a high detection limit. Moreover, the reaction rate for derivatization from 20 ml of water was slow.

Several modifications of the procedure were investigated to alleviate these problems. First an in-line chromatographic separation of derivatized analytes from interferences was developed (14,15) to separate fatty acids from the PFB ester of 2,4-Dichlorophenoxy acetic acid (2,4-DiClPAA). Second benzyl (Bz) esters were prepared. Since Bz esters of the fatty acids were not electrophoric whereas Bz derivatives of the halogenated target analytes were readily detected by the electron capture detector this derivatization procedure was expected to reduce the interferences (15). Finally, extraction from large volumes was

investigated in order to increase the amount of analyte relative to the interferences generated from the fatty acids in the background. Due to the concentration of analyte on the resin, it was possible to test different methods of forming the Bz and PFB derivatives on the resin.

EXPERIMENTAL:

Apparatus: The derivatives of the analytes were determined on a Helwett-Packard (H-P) 5710 or 5790 gas chromatograph equipped with a pulse linearized electron capture (ECD). The 5710 instrument was equipped with a 15 m DB-1 megabore column with an inner diameter of 0.53 mm and a film thickness of 1.5 micrometers. The 5790 instrument was equipped with a 30 m DB-1 J & W fused capillary column with an inner diameter of 0.32 mm and a film thickness 0.25 micrometers. The output of the detectors was monitored on H-P 3390A recording integrators. Hydrogen was used as a carrier gas for the megabore column the flow rate was set at 4 mL/min and for the capillary column it was set at a linear velocity of 62 cm/sec at 180°C and 10 % methane in argon was used as a make-up gas at a flow rate 15 ml/min.

Reagents: Pentafluorobenzyl bromide and BzBr were purchased from Caledon Laboratories, Georgetown, Ontario, and from Aldrich Canada respectively. The macroreticular resin, XAD-2, a cross-linked copolymer of styrene/divinylbenzene was obtained from BDH Laboratories, Toronto, Ontario and was cleaned and stored as previously described (13). Florisil, basic alumina, disposable 1 ml Supelclean columns for semi-preparative chromatography and a vacuum module were also purchased from Supelco (Canada) Oakville Ont. Solvents were purchased from the usual commercial suppliers, such as Fisher, BDH and Aldrich Canada. Pure analytes were obtained from the E.P.A Repository.

All the glassware was silylated by standard procedures. Glassware and plasticware was washed with methylene dichloride, methanol, acetonitrile and dried prior to use.

Preparation of PFB and Bz Derivatives: Derivatives of the pure analytes were prepared by stirring of the organic acid in acetone with PFBBr or BzBr with K_2CO_3 as the base. Reaction work-up consisted of evaporating the acetone, extracting the residue with CH_2Cl_2 and finally washing the organic phase with distilled water. The PFB products were purified by thin-layer chromatography.

Derivatization and Isolation: Three hundred mG of XAD-2 was added to glass 25X200 mm screw cap vials and wetted with 300 μ l of acetonitrile. The vials were charged with 40 mL unbuffered tap water containing C^{14} radiolabelled 2,4-DiClCPAA and corresponding to 5 nG/ml. The aqueous phase was acidified with 0.1 N HCL and the reaction mixture was shaken for 30 minutes. The resin was

reaction rate was calculated from the rate of disappearance of the radiolabel from aqueous solution.

RESULTS AND DISCUSSION:

Under the described conditions, adsorption of 2,4-DiClPAA from 40 ml volumes was time dependent with a half life of 8 minutes. Thus effective adsorption onto a resin bed of 300 mg required 30 minutes. This slow rate of adsorption due, in part, to the hydrophilicity of the analyte but also the high ratio of liquid to solid phase. Once the analyte had been adsorbed the resin was isolated and two different reaction techniques were investigated.

In the first technique ultrasonication was used to agitate the solution. Since the resin with the adsorbed analytes was isolated the ratio of liquid to solid could be adjusted at will and kept as small as required. Both PFBBR and BzBr were used for the derivatization. In a reaction time of two hours the yield of the PFB ester was 60%. As in previous studies the reaction yield for Bz ester lower (40%) since BzBr is less reactive than PFBBR. These are comparable to those obtained by shaking; although it is interesting that the reaction rate for derivatization with BzBr appears to be faster than that using the classical agitation technique (14,15). Use of ultrasonication has a particular advantage - capping is not required as tubes can be left open to the atmosphere and in a vertical position. This removes one step from the procedures, eliminates the need for teflon lined caps and losses due to leaking tubes if the seals are not set properly. It would be particularly advantageous for development of automated techniques where capping would be a problem.

In the second technique it was possible to take advantage of the fact that in previous work we had demonstrated a chemical drying technique using acidified DiMP (14,15) as a water scavenger. Since after adsorption the resin was saturated with acidified water the surface could be dried simply by adding the neat reagent with the adsorbed water supplying the required proton to catalyze the conversion of DiMP and water into methanol and acetone. Once the surface was dry the PFB ester was formed via base catalyzed esterification - a reaction that requires anhydrous conditions. This was carried out simply by addition of a solution of PFBBR and DiPEA in CH₃CN. limiting the volume of this solution to the pore volume of the resin there was little loss of analyte from the surface. Since there was no water to protonate the highly hindered base the acid 2,4-DiClPAA was ionized in-situ and was thus derivatized. In this procedure the resin functioned simply as a support for the analyte, reagent and base. The reaction rate under these conditions is considerably faster and even for BzBr a yield of 47 % was obtained in 15 minutes.

The in-line chromatographic clean-up eluted 80-90% of the PFB esters of the fatty acids in the 25% toluene/hexane fraction. The

acid concentration could be quite high and in addition plasticware used in sample preparation can also contribute interferences (17). Thus simply cleaning laboratory equipment will only partially resolve the problem and a more generic solution to the background problems are required.

Formation of the Bz rather than the PFB ester produced some improvement in the background. The reaction rates for this reaction were slower than for pentafluorobenzoylation. In addition, the limitations to sensitivity arose from contaminants of plasticware particularly from low levels of PFB esters that was due to re-use of the cartridges.

SUMMARY: Pre-adsorption of analytes can be used to simplify the procedure by the allowing agitation of an aqueous reaction mixture by ultrasonication. In addition the use of a chemical drying procedure allows of XAD-2 as a support for a base catalyzed reaction. Interferences can partially reduced by in-line chromatography or by treatment of glass-ware with oxidizing agents. The latter approach can only reduce those interferences present in the laboratory; the former approach using more sophisticated instrumentation would reduce those interferences from fatty acids that must be present in the environment.

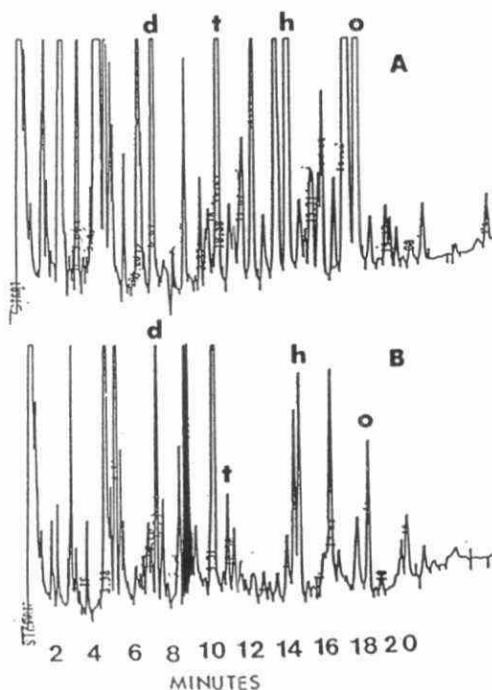
REFERENCES:

1. Federal Register Part VIII. Environmental Protection Agency 58 (1984).
2. Hall D. Ministry of the Environemnt of Ontario. Private communication
3. Bertrand M.J., A.W. Ahmed, B. Sarrasin and V.N. Mallet. Anal. Chem. 59:1302-1306 (1987).
4. C.F. and S.A. Schuette "Contemporary Practice of Chromatography" Elsevier (Toronto) 1984 Ch. 7.
5. Xie K-H, S. Colgan, I.S. Krull. J. Liq. Chromatogr. 6 (s-2):125-151 (1983).
6. Colgan S. and I.S. Krull. Anal. Chem. 58:2366-2372 (1986).
7. Rosenfeld J.M., G.M. Brown, C.H. Walker and C.H. Sprung. J. Chromatogr. 325:309-313 (1985).
8. Rosenfeld, J. M., M. Mureika-Russell and S. Yeroushalmi. J. Chromatogr. 358: 137-146, (1986).
9. Rosenfeld, J.M., M.C. Orvidas and O. Hammerburg. J. Chromatogr. 378:9-17, (1986).

10. Rosenfeld, J.M., R. McLeod, R.L. Foltz. Anal. Chem. 58:716-721 (1986).
11. Rosenfeld J.M. Love M., Mureika-Russell M. J. Chromatogr. 489:263-272 (1989).
12. Rosenfeld J.M., Y. Moharir and S.D. Sandler. Anal. Chem. 61:925-928 (1989).
13. Rosenfeld J.M., A. Phatak and M. Mureikka-Russell. J. Chromatogr. 283:127-135 (1984).
14. Rosenfeld J.M. Matthew-Ahlang, F. Proceedings of the Technology Transfer Conference: Environment Ontario. (1988) p 69.
15. Rosenfeld J.M., Y. Moharir and Matthew-Ahlang, F. Proceedings of the Technology Transfer Conference: Environment Ontario. (1989) p 287.
16. Greving, J.A., J.H.G. Jonkman, De Zeeuw. J. Chromatogr. 148:389-395, 1978.
17. Junk G.A., M.A. Avery and J.J. Richard. Anal. Chem. 60:1347-1350 (1988).

Figure 1. GC/ECD traces of eluates from the XAD-2 reactor bed - Florisil - Silica Gel link: A) fatty acid fraction and B) chlorophenoxyacetic acid fraction. Peak corresponding to PFB ester of 2,4 Dichlorophenoxy Acetic Acid is darkened.

PFB esters of: d = dodecanoic acid; t = tetradecanoic acid; h = hexadecanoic (palmitic) acid; o = octadecanoic (stearic) acid.



BIAS DUE TO SAMPLING GROUNDWATER AND SURFACE WATER FOR TRACE ORGANIC CONTAMINANTS. Part 1. Losses Due to Volatilization.

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INTRODUCTION

Contamination of surface and groundwater by synthetic organic compounds is a major environmental concern in Ontario and most industrialized areas. In sampling natural waters for organic contaminants, two main sources of negative bias are recognized, loss of volatile compounds by partitioning into the atmosphere and loss of hydrophobic compounds by sorption onto synthetic polymers used in the construction of wells and samplers. Considerable research has been conducted at the Waterloo Centre for Groundwater Research and by numerous other research groups into the magnitude and the means to minimize these biases.

It is generally recognized that compounds with Henry's law constants greater than $0.001 \text{ (atm m}^3 \text{ / mol)}$ have the potential to be volatilized if the solution is exposed to the atmosphere during sampling and analysis. Most common organic groundwater contaminants fall into this category, and evaluating the potential for volatilization loss has been the object of several groundwater sampling studies. Barker and coworkers [1,2] evaluated the potential for volatilization and sorption losses when using multilevel piezometers and several other sampling devices. Ho [3] studied the effects of transport line material, pumping rate and sample lift height on the recovery of volatile organics in water with a peristaltic pump. Barcelona et al [4] tested a large number of samplers in an attempt to evaluate the effectiveness of various sampling mechanisms. Pearsall and Eckhardt [5] evaluated several common samplers and the effects of variations in sampling procedures and details of set-up. These studies have demonstrated that: 1) the potential for significant negative biases exists with common sampling devices, 2) the biases appear to be caused by volatilization (and by sorption in some cases), and 3) some consistency among studies has been found in the relative effectiveness of various samplers and sampling mechanisms.

Recently, particular emphasis has been placed on the problem of sampling gas-charged groundwater such as can be encountered in landfill leachate plumes and natural gas associated formations, for example. Pankow [6] provided a theoretical basis for estimating the artifacts due to bubble formation during sampling. Barker and Dickhout [2] tested the effectiveness of a positive displacement pump, an inertial lift pump and a peristaltic pump in sampling gas-charged water for volatile organics. Their finding that the peristaltic pump induced the greatest negative bias qualitatively agrees with theory; however, a consistent correlation between relative loss and Henry's constant was not observed, although only a narrow range of volatilities were represented by the compounds used.

It is evident that further research is required to realize the goal of quantitative estimation of sampling bias due to

volatilization. The present study incorporates several improvements in design over the previous study by Barker and Dickhout [2]. Larger Henry's constant values are represented by the organic contaminants, and methane was included. Dissolved carbon dioxide concentrations were measured in order to establish a link with theory. In addition, the experimental well was constructed of stainless steel instead of PVC, eliminating the possibility sorption losses in the well; the well contained a sampling port at the bottom for obtaining representative control samples. Finally, six samplers were evaluated at two concentration levels, making this a more comprehensive study.

METHODS

An artificial well was installed in a stairway at the University of Waterloo Centre for Groundwater Research. The well essentially consisted of a 6" diameter stainless steel pipe, 32' in height with a sampling port located near the bottom. The well was filled and drained at the bottom with an air-driven pump connected to a stainless steel reservoir. Gas-laden artificial groundwater, approximating that in an aquifer contaminated by low-level organics, was made as follows. A 90 litre volume of tap water containing 3.4 g/L sodium bicarbonate was prepared in the reservoir and its pH was adjusted to 9.0 with 1 N NaOH. The water in the reservoir was spiked with: 1) a saturated solution of methane in water, and 2) a methanolic stock solution containing benzene (366.5 ppm), toluene (723.3 ppm), trichloroethene (610.7 ppm), trans-1,2-dichloroethene (262.1 ppm), and 1,1-dichloroethene (254.0 ppm). The spiking volumes that were used in the experiments are given below.

Experiment	Concentration Level	Volume (mL)	
		Methanolic Stock	Methane Water
1-2	high	9.00	4000
1-1	low	0.45	415
2-2	high	9.00	4000
2-1	low	0.45	415
3-2	high	9.00	4000
3-1	low	0.90	1000
4	high	9.00	4000

After stirring, the solution in the reservoir was pumped through a port in the bottom of the well along with 2 L of a 10 % HCl solution, thus converting the bicarbonate ions to carbon dioxide. Since the bicarbonate and HCl solutions were proportionally mixed as they entered the bottom of the well, some of the carbon dioxide was liberated, but most was kept in solution by hydrostatic pressure in the well.

The following sampling systems were evaluated: a double check-valve stainless steel bailer (BAIL), a peristaltic pump (PER), a WaTerra inertial pump (WAT), an IEA syringe sampler (SYR), a Well Wizard bladder pump (WIZ), and a Solinst double-valve purge/sample pump (SOL). In each experiment, the high capacity foot-valve WaTerra (model D-32) and one or two other samplers were tested, and the water was sampled using the control port at the bottom of the well. In experiment 4, the high capacity WaTerra was compared with the smaller WaTerra (model D-16). Approximately the same well depth was sampled by all of the samplers.

Five replicate samples were taken with each sampler and from the control port. Upon collecting a sample, two 60 mL hypovials were immediately filled to overflowing and capped with teflon-faced septa. The hypovials were stored underwater at approximately 4 °C and the contents were analyzed within five days. The organic contaminants (benzene, toluene, TCE, 1,2-DCE, 1,1-DCE) were determined using one of the hypovials from each pair, and the other was used for determining the methane and carbon dioxide concentrations. The organic contaminants were determined in the headspace created in the hypovials when 15 mL of sample was replaced with an equal volume of laboratory air. After equilibration, the headspace was injected directly into a gas chromatograph fitted with a photoionization detector. Methane and carbon dioxide were also determined by static headspace gas chromatography with FID and TCD detectors. The relative standard deviations for five replicate determinations of the gases and the organic contaminants ranged from 4 to 8 %.

RESULTS

The data are summarized by experiment in Table 1, which gives the average concentrations for each group of five replicate samples. Percentage losses were calculated from the data of Table 1 by the formula

$$\text{Loss}(i,j,k) = -100 \times (\text{Sampler}(i,j,k) - \text{Control}(i,j)) / \text{Control}(i,j)$$

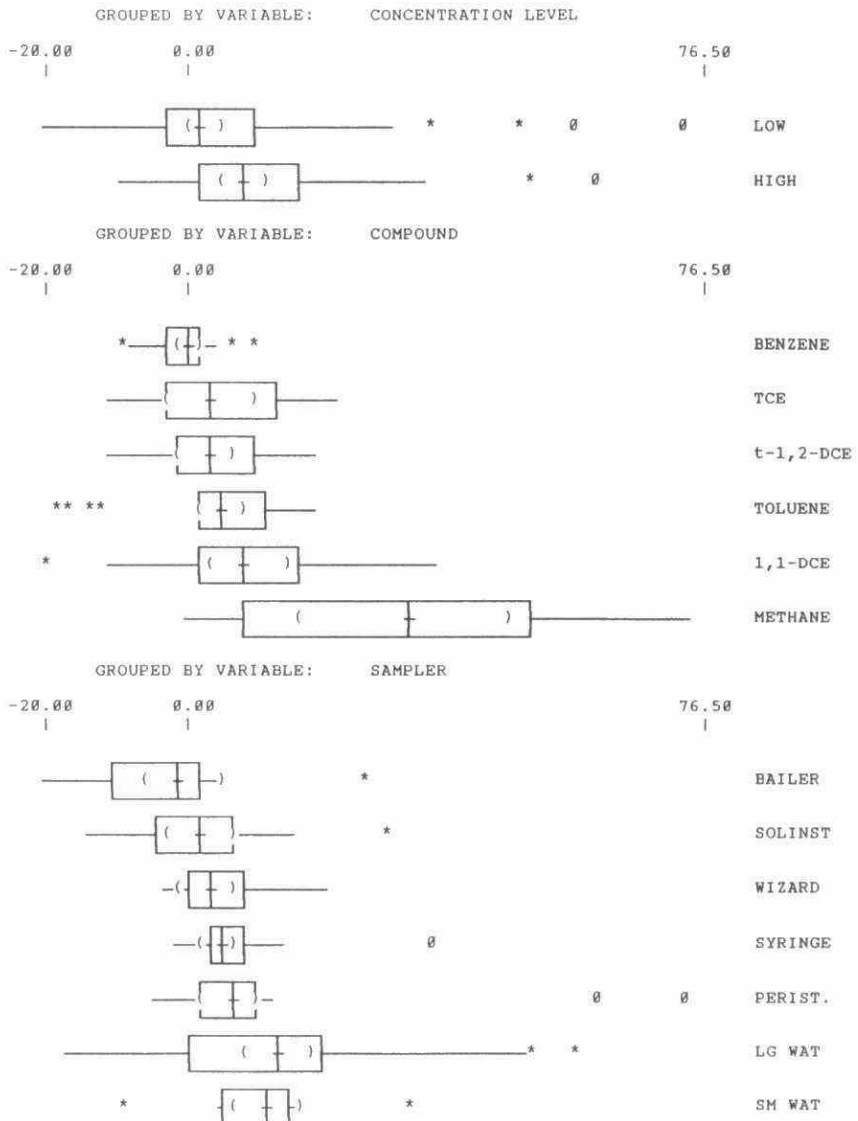
$\text{Sampler}(i,j,k)$ is the mean concentration for compound i , concentration level j , and sampler k . Similarly, $\text{Control}(i,j)$ is the mean concentration for the appropriate control sample. The percentage losses have been analyzed by the box plot technique [7]. In making statistical comparisons, a significance level of 0.05 is used throughout. Figure 1 depicts the percentage losses obtained by one-way classification according to compound, sampler and concentration level. Significantly positive biases are notably absent in all three categories. The difference in bias between the high and the low concentration levels is barely significant, with the high concentration bias being about 6 % more negative than the low concentration bias. The percentage loss incurred at the low level is not significantly different from zero. The percentage of compound lost by volatilization should not be affected by the concentration of the compound [6].

Considering next the box plots for the organic compounds, methane shows the greatest median loss, and this is significantly greater than the medians for the other compounds. Methane also shows a significantly greater variance. The methane losses are significantly correlated with the CO_2 losses (Figure 2), which suggests that volatilization is responsible for the methane losses. The other compounds are not significantly correlated with CO_2 , and this is consistent with the fact the Henry's constant for methane is larger than those for the other compounds. The Henry's constants ($\text{atm} \cdot \text{m}^3 / \text{mol}$) for the compounds are [6]: methane, 0.676; 1,1-dichloroethene, 0.19; t-1,2-dichloroethene, 0.067; trichloroethene, 0.0091; toluene, 0.0067; benzene, 0.0055. The order of increasing loss among the compounds approximately parallels the order of increasing Henry's constant. Most of the variability among compounds is due to the contrast between methane and the other compounds. The 95 % confidence intervals (indicated by parentheses in the box plots) for the other compounds overlap extensively; for three

Table 1. Mean concentrations ($N=5$) for each experiment. Concentrations are given in 10^{-6} g/L except for CO_2 which is given in g/L.

Expt.	Sampler	Compound						
		BEN	TOL	TCE	1,2-DCE	1,1-DCE	METH	CO_2
1-2	CONT	16.8	33.6	26.5	10.8	10.4	408	1.24
	WAT	16.3	31.2	24.0	10.0	9.6	260	0.96
	BAIL	16.0	31.8	25.2	10.5	10.5	292	1.10
	PER	15.8	29.6	23.1	10.1	9.1	153	1.05
1-2	CONT	0.93	1.84	1.39	0.48	0.35	36.5	1.11
	WAT	0.91	2.10	1.42	0.47	0.32	14.6	0.97
	BAIL	0.91	2.14	1.50	0.52	0.42	33.6	0.81
	PER	0.91	1.58	1.42	0.45	0.34	8.6	1.01
2-2	CONT	21.7	42.6	35.3	14.4	13.3	232	1.24
	WAT	19.1	35.3	27.0	11.5	8.8	152	1.06
	WIZ	21.1	39.9	33.1	13.6	11.7	215	1.30
2-1	CONT	1.1	2.13	1.95	0.63	0.45	32.5	1.43
	WAT	0.99	1.98	1.60	0.56	0.37	16.0	1.13
	WIZ	1.1	1.83	1.95	0.55	0.35	31.3	1.35
3-2	CONT	19.4	39.4	29.1	13.6	12.4	426	1.97
	WAT	18.7	33.5	24.6	10.8	9.6	198	1.51
	SOL	20.3	36.6	29.7	12.1	11.2	347	1.90
3-1	CONT	2.13	3.60	3.19	1.09	0.76	95.0	1.94
	WAT	2.14	3.96	2.97	1.11	0.82	38.9	1.19
	SOL	2.11	3.99	3.07	1.04	0.72	64.3	1.66
	SYR	2.0	3.2	3.0	0.92	0.46	86.8	1.96
4	CONT	21.3	38.7	36.3	13.1	11.0	382	1.96
	LG.WAT	20.5	30.2	27.4	10.6	8.85	247	1.59
	SM.WAT	22.7	32.5	30.2	12.0	9.54	248	1.76
	SYR	20.4	36.1	33.9	12.7	10.1	338	1.82

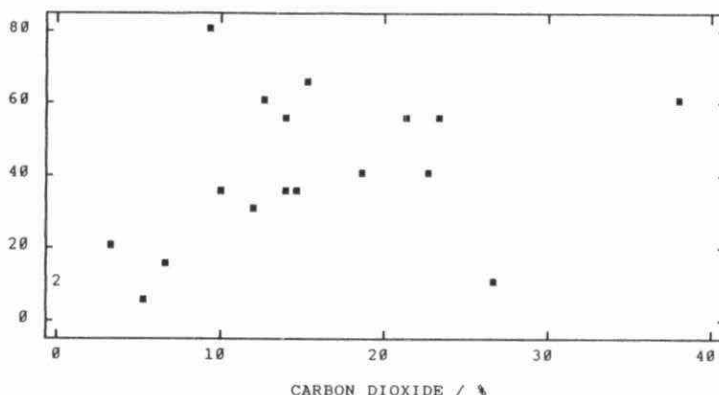
Figure 1. BOX PLOTS OF PERCENTAGE LOSS (N = 108)



of the compounds, the median biases are not significantly different from zero.

Figure 2. SCATTERPLOT OF PERCENTAGE LOSS, METHANE VERSUS CARBON DIOXIDE

METHANE / %



The variability associated with sampler bias, expressed as the standard deviation of the medians, is 4.3 %. This is comparable to the analytical variability for replicate analyses of the same sample. The sampling losses increase in the order: BAIL, SOL, WIZ, SYR, PER, WAT. The 95 % confidence intervals overlap extensively, so the order is not well-defined. The losses for the SYR, PER and WAT samplers are significantly different from zero, while those for the BAIL, SOL and WIZ samplers are not significantly different from zero or from each other. The losses for the large and small WAT samplers are indistinguishable from each other and are significantly greater than those for the BAIL, SOL, WIZ, and SYR samplers.

The box plots provide a robust (nonparametric) one-way analysis of variance. A two-way anova is more powerful, because the error mean square is reduced by taking into account the variance due to the other factor, but the experimental data violate the homogeneity of variance assumption. As mentioned previously, methane shows a larger variance. The simpler method of analysis (box plots) was used, because it is less prone to type II error (concluding that a significant difference exists when it does not). The methane data appear as outliers in the box plots for the samplers, thus exerting little influence on the medians and on the 95 % confidence intervals. This was verified by comparing the box plots in Figure 1 with those obtained when the methane data was deleted. The sampler losses depicted in Figure 1 are therefore representative for compounds having Henry's law constants smaller

than $0.2 \text{ atm m}^3 / \text{mol}$.

The losses for methane indicate a somewhat different sequence for the samplers from that indicated by the other compounds. In order of increasing methane loss, the sampler sequence is SOL, SYR, BAIL, WIZ, WAT, PER. However, a one-way analysis of variance indicates that the sampler means are indistinguishable. Because the degrees of freedom for the test is small, it is not possible to discriminate small differences between sampler means for individual compounds. More replication would be necessary to test hypotheses concerning the relative effectiveness of the sampling devices for particular compounds. This provides some justification for pooling the compounds in the test for sampler effects, and further justification is provided by the fact that biases are not significantly correlated among the compounds, i.e. the assumption of independent errors is not violated.

The percentage losses computed from the data of Table 1 were also used to estimate the random variability associated with sampling. The sampling variability, expressed as a standard deviation, was computed for each compound by taking the square root of the mean square error of a one-way analysis of variance for sampler effects. The high and low concentration data were pooled, yielding 12 degrees of freedom for the estimate. The variabilities for benzene and methane are 4 % and 33 %, respectively, and the middle compounds fall into the range of 11 to 17 %. The sampling variabilities tend to increase as the Henry's law constants increase. Because each datum is the mean of five replicate samples taken with a given sampler in a single day's experiment, the variability for single samples is greater. Assuming that the variability for samples taken on a single day is the same as that for samples taken on different days, the sampling variability for single samples is estimated to be in the range of 20 to 40 % for the middle compounds. Therefore, the systematic variability associated with the samplers (4.3 %) is small relative to the random variability associated with taking replicate samples with a given sampler. It is also worth noting that the sampling device may introduce less bias than the laboratory performing the analysis. This is demonstrated by the results of a recent interlaboratory comparison for the analysis of low molecular weight aromatic compounds, e.g. benzene, toluene, etc. (R. Dickhout, unpublished data). A relative standard deviation of 28 % was obtained for the 10 participating commercial laboratories, and this is considerably larger than the 4.3 % RSD obtained for the seven sampler medians.

DISCUSSION

The question of whether or not volatilization is the mechanism responsible for the observed losses of organic compounds can now be discussed. The fact that methane showed the greatest percentage losses is consistent with the relative magnitudes of the Henry's constants. Most of the variation in the biases for the compounds and in the Henry's constants is due to the contrast between methane and the other compounds. The fact that the methane losses are significantly correlated with the CO_2 losses (Table 1) strongly suggests that methane bias is due to volatilization. Recent sampling studies carried out in this laboratory (R. Dickhout, unpublished data), have revealed that substantial losses occur during

the well filling procedure, apparently caused by the effervescence produced when the sodium bicarbonate and HCl solutions are mixed.

Substantial amounts of carbon dioxide were lost during the sampling process. From the median percentage loss (15 %, Figure 2) and the typical concentration for CO₂ in the control samples (1 g/L, Table 1), it is estimated that about 0.07 mL of carbon dioxide gas was lost to the atmosphere per mL of solution. Pankow [6] has derived equations to predict sampling losses due to spontaneous bubble formation in gas-charged waters. Assuming that carbon dioxide gas bubbles were produced during sampling, Pankow's eq 11 predicts percentage losses ranging from 1.6 % for benzene to 86 % for methane. The predicted losses are, on average, about a factor of 2 greater than the observed percentage losses (Figure 1). However, gas stripping of volatile compounds is not likely to be the mechanism responsible for the observed losses. The estimated in situ gas pressure (fugacity) for dissolved carbon dioxide in the well is 0.68 atm. Spontaneous formation of gas bubbles cannot occur unless the ambient pressure is reduced to a value smaller than the in situ gas pressure plus the vapour pressure of water. The peristaltic pump is the only sampler which could cause a substantial reduction in the ambient pressure. It is therefore postulated that the volatile compounds were lost by mass transfer at the air-water interface. The lack of an exact correlation between percentage loss and Henry's constant value may be due to the possible non-equilibrium nature of the postulated mechanism or due to the fact that the losses were small relative to experimental error.

Because it is a gas at room temperature and pressure, methane has a much greater potential for volatilization than for sorption by synthetic polymers. The other compounds would have greater potential for sorption relative to methane because they are liquids. Interestingly, the order of increasing Henry's constant is similar to the order of decreasing solubility in water for the compounds. A compound's solubility in water is correlated with its polymer-water partition coefficient, so the tendency for sorption losses would be expected to approximately parallel that for volatilization losses among compounds having a narrow range of boiling temperature, which is the case for the liquids used in the experiments. Some of the samplers used in this study expose the sample to synthetic polymers. For example, plastic transfer line tubing was used with the WAT, WIZ, PER and SOL samplers. Exposure to polymeric materials is thought to be minimal for the BALL and SYR samplers. The order of bias among the samplers does not appear to be correlated with the degree of exposure to organic polymers, however.

The relative performance of the samplers seems to be consistent with the results of previous studies [2,4,5] which show that sampler bias tends to increase in the order: grab samplers, positive displacements pumps, suction pumps (PER). The inertial lift pump (WAT) has not often been included in previous studies. The one published evaluation [2], indicated that the WAT sampler performed as well as the WIZ sampler and better than the peristaltic pump. In the present study, the WAT sampler did not perform as well as the other samplers. This apparent discrepancy may reflect differences in the way the samplers were used in the two studies, since it was previously shown [3,5] that factors such as rate of pumping and sample lift height can influence bias.

POYNUCLEAR AROMATIC HYDROCARBONS IDENTIFICATION

USING GC/FT-IR AND PAIRS

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ABSTRACT

Gas chromatography/Fourier transform infrared (GC/FT-IR) spectra of 33 polynuclear aromatic hydrocarbons (PAHs) have been measured at the Ontario Ministry of the Environment. High signal to noise ratio (SNR) vapor phase spectra have been obtained for the majority of the PAHs, a lower SNR being obtained for 4 PAHs with very low vapor pressures. A vapor phase infrared spectral library has been created which makes the identification of PAH target compounds possible by GC/FT-IR. The spectral region 700 to 1000 cm^{-1} containing the C-H and $-\text{CH}_2$ out-of-plane and C-C in-plane bending modes demonstrate a unique spectral feature for each PAH. It is possible to distinguish between a group of PAH isomers using only the information from this spectral region. The PC based version of the program for the Analysis of InfraRed Spectra (PAIRS[®]) is employed and an interpretation tree specific for PAHs is at the preparation stage to make "functional group frequency" screening of PAHs possible.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are a major class of chemical compounds with extremely complex structures. Due to large variability in isomer formation several hundred different types of PAHs can exist. For example, for PAH's containing 6 aromatic rings, 82 isomeric configurations are possible. Since the toxicity, carcinogenicity, and mutagenicity of different PAH isomers can be very different, the ability to distinguish these isomers for environmental assessment and consequently, for remedial actions is important. The Ontario Ministry of the Environment (MOE) has been analyzing 37 targeted PAHs at the Trace Organics Section (TOS) of the Laboratory Services Branch (LSB)⁽¹⁾. These PAHs had been selected based on their occurrence in the province of Ontario. The spectra of only 13 of these 37 PAHs are in the Nicolet/Aldrich enhanced U.S. Environmental Protection Agency infrared vapor phase library

(EPA library) ⁽²⁾. The lack of the other 24 PAH spectra in the EPA library complicates the identification of the gas chromatograph/Fourier transform infrared spectra (GC/FT-IR) of these PAHs.

The applicability of gas chromatography/ Fourier transform infrared spectroscopy (GC/FT-IR) to environmental sample analysis containing some PAHs has been demonstrated by several groups ⁽³⁻⁵⁾. In these studies only a few of the PAHs listed in Table 1 have been investigated. The use of the combined data from GC/FT-IR and GC/MS for sample analysis has also been demonstrated ^(6,7), and data obtained from directly linked GC/FT-IR/MS have been reported ⁽⁸⁾. These studies have demonstrated the need for vapor phase infrared spectral data bases that include PAHs containing four or higher aromatic rings ⁽⁶⁾. The use of GC/MS for identification of PAHs is a powerful technique for obtaining molecular structural information but most conventional electron impact ionization mass spectrometers (EI/MS) can lead to identical fragmentation of isomers and thus to identical mass spectra. Matrix isolation infrared spectrometry (MI-IR) has also been applied for PAH identification ^(9,10), in mixtures containing up to 5 components and gas chromatography matrix isolation (GC/MI-IR) spectra of several PAHs have been recorded ⁽¹¹⁾. The quality of MI-IR spectra is dependent on the type of matrix used and the ratio of matrix to sample. Both these factors can cause infrared band splitting and band shifts and can change full width at half height (FWHH) of some bands.

In order to increase our capability for identification of PAHs and in order to distinguish between their many isomeric configurations we have measured the GC/FT-IR spectra of 33 PAHs and created a vapor phase infrared spectral library. These spectra reveal that the spectral region from 700 to 1000 cm^{-1} containing the aromatic C-H and $-\text{CH}_2$ out-of-plane and C-C in-plane bending modes can provide unique information for each isomeric compound.

EXPERIMENTAL

A. CHEMICALS.

Solutions of PAHs were prepared by dissolving 1-2 mg of each standard in 1 ml of

toluene. Benzo[a]anthracene, benzo[b]anthracene (80% purity (UV)), benzo[a]fluorene (>98% (HPLC)), benzo[ghi]perylene, coronene (97% (HPLC)), 9,10-dimethyl anthracene (97% (HPLC)), dibenzo[a,c]anthracene (>97% (UV)), dibenzo[a,h]anthracene, 7,12-dimethyl-benz[a]anthracene, 2-methyl anthracene (>99% (HPLC)), triphenylene (>98% (HPLC)) and Perylene (>99% (HPLC)) were purchased from Fluka AG, chem.Fabrik. Benzo[c]phenanthrene (Community Bureau of References), anthracene (Aldrich, 99.9%), benzo[a]pyrene (Aldrich, 98%), benzo[b]fluoranthene (Supleco, Inc.), and benzo[k]fluoranthene (Supleco, Inc. 99%) were also used for sample preparations. 9-Methyl anthracene, 3-methyl cholanththrene, O-terphenyl, M-terphenyl and P-terphenyl were obtained from Eastman Kodak Co. and acenaphthene, acenaphthylene, fluorene, fluoranthene, and phenanthrene were obtained from EPA Research Triangle Park.

B. INSTRUMENTATION

A Nicolet 55X (Madison, WI) FT-IR spectrometer equipped with a 0.1 mm HgCdTe cryogenic detector and an air cooled nichrome wire source was used to measure the GC/FT-IR spectra. A Hewlett-Packard 5890 (Palo Alto, CA) gas chromatograph equipped with a splitless injector, a wide bore column (cross-linked methyl Silicon Gum, 25m x 0.32mm x 0.17 micrometer film thickness) and a flame ionization detector were used for the separation. The dimensions of the GC/FT-IR light pipe interface used were 12 cm x 0.1 cm. Using the above combination, interferograms were collected at a sampling rate of 50 kHz and an optical retardation of 0.125 cm. Either the Gram-Schmidt orthogonalization or the ChemiGram methods were used to reconstruct a real time chromatogram from the interferogram and the low resolution infrared spectra ⁽¹²⁾. At the end of the experiment the appropriate number of the interferograms were coadded and Fourier transformed to obtain the infrared spectrum of each compound.

For the preliminary analyses of PAHs the LSB routine method PAAPAH-AC8NCQ.21 ⁽¹⁾ was used. This resulted in obtaining GC/FT-IR spectra of low signal-to-noise ratio (SNR). This method was modified in several ways to enhance the spectral SNR. A wide bore column was used to make an injection of a higher volume of the sample possible. We also employed

on-column injection instead of split injection without masking the lower boiling PAHs (e.g. tetralin and naphthalene) under the solvent band and no make up gas was used to prevent analyte dilution in the light pipe.

The signal of the cryogenic Hg-Cd-Te detector decreases with increasing temperature of the light pipe. This phenomenon is attributed to (1) the temperature induced changes in the reflectivity of the gold coating inside the light pipe and (2) the masking of the modulated infrared signal from the interferometer by the unmodulated thermal radiation from the light pipe. For our detector, we observed a loss of about 45% of the signal by increasing the light-pipe temperature from 50 to 290°C. The boiling points of the PAHs can vary from approximately 200 to 600°C. Hence, the light pipe had to be operated at its optimum temperature which is about 285°C throughout our investigation. This represents a loss of about 45% of signal intensities in our experiments.

RESULTS

The sensitivity of the GC/FT-IR was first evaluated using the following experimental conditions. The light pipe temperature was set at 280°C, the column head pressure was varied from 5 to 20 psi and the GC/FT-IR spectra of a solution of dimethyl phtahlate (DMP) in toluene was recorded. For 60-nanogram DMP injected at a column head pressure of 15 psi, we could achieve a SNR of 10 for the most intense band in the spectrum. Lower detection limits have been reported in the literature, but the operating conditions have been very different in those studies. The light pipe temperature in those cases has been set between 170 to 240°C. From the relationship between the signal of the detector and the light pipe temperature it becomes clear that we will have a detection limit of 30 nanogram if we use a light pipe temperature of about 200°C.

In the preliminary work the vapor phase spectra of 10 PAHs were collected. These 10 PAHs are among the 13 PAHs for which vapor phase spectra exist in the EPA library. The

temperature of the light pipe and the transfer line were set at 285°C, and the GC was temperature programmed from 80 to 300°C with an initial two minutes hold at 80°C. The GC oven temperature was ramped at a rate of 8 to 20°C/min, depending on the type of the sample, to 300°C. The quality of our spectra were either equivalent or in some instances, superior to those in the EPA library. Table 1 gives the list of these compounds (numbers 1 to 10). Under the same experimental conditions we obtained the GC/FT-IR spectra of the other PAHs (compounds number 11 to 33). The spectrum of each compound was measured at least three times to obtain the best quality possible. When necessary, solutions were concentrated by evaporating some of the solvent. Attempts to obtain the infrared spectra for Picene and Coronene were unsuccessful. Picene has a very low solubility in toluene or any other organic solvent at room temperature. Coronene has an estimated boiling point of about 590°C. Chrysene, Dibenzo[a,h]Anthracene, Perylene and Benzo[ghi]Perylene have relatively lower solubility than other PAHs in organic solvents which resulted in obtaining spectra with lower SNR.

These spectra have been transferred from the Nicolet 620 computer to the MS/DOS system in the Spectral Calc format. Thus forming part of the Ontario Ministry of the Environment vapor phase infrared spectral library of the PAH standards. This library will be expanded with other types of PAHs such as alkyl and halogen substituted, nitro-PAHs and heteroatom containing PAHs.

The creation of this library allowed us to attempt to identify the components of a mixture. The experimental condition were as before except for the use of a DB-5 25m x 0.33 i.d. x 1.0 micrometer film thickness capillary column. A sample of standard solution of PAHs mixture (3 microliters) was injected into the GC column and a GC/FT-IR analysis was carried out. Figure 1 shows the out put obtained from FID and the Gram-Schmidt reconstructed chromatograph for this analysis. After Fourier transformation of the interferograms the spectra were searched using the EPA library which has a total of 5010 entries. For those components whose infrared spectra are in the library, the correct identification was provided. For eight components for which there is no vapor phase spectra in the library, four best matches were given, all of which were

incorrect. We were able, however, to identify correctly these PAHs using the newly created library. This experiment emphasizes the importance of creating an MOE library of PAH infrared spectra which enables the identification of the target PAHs encountered in the province of Ontario.

DISCUSSION AND CONCLUSION

Table 1 lists the PAHs investigated in the current study and the infrared absorption bands with significant intensities in the region 650 to 4000 cm^{-1} . Figure 2 shows the GC/FT-IR spectra of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]pyrene and perylene, five PAH isomers with five rings and molecular weight of 252.3, in the spectral region 650 to 4000 cm^{-1} . Several changes in the appearance of infrared spectra, such as frequency shifts and changes in the relative intensities, are associated with changes in the physical state of a compound. For example, the infrared bands associated with the C-H aromatic stretching shift toward higher frequencies and those associated with C-H out-of plane bending modes often shift toward lower frequencies as the state of the matter changes from condensed to vapor state. Also, some active modes in the spectra of the condensed phase become inactive in the gas phase or show a considerable decrease in intensity. This is observed for the most of the vibrational modes associated with C-H in plane bending and CC stretching modes. The simplicity of the vapor phase spectra (see Figure 2) could be considered advantageous for fast identification of the components of a complex environmental sample mixture.

While we are in the process of accumulating more vapor phase infrared spectra to enhance our capability for identification of the PAHs, it is also recognized that due to the large variability of PAHs which can be present in complex environmental sample mixtures other methods for fast identification must be explored. Program for the Analysis of InfraRed Spectra (PAIRS) which was originally developed by Woodruff and Smith ⁽¹³⁾, has been implemented recently in our laboratory on a 386 based personal computer running MS/DOS ⁽¹⁴⁾. The information flow in

PAIRS* is similar to the reasoning a chemist uses in interpreting spectral data. The computerized interpreter requires as input the spectrum, supplemental information and interpretation rules. As output, the program prints probabilities for each functional group under consideration. We have used PAIRS* to interpret the PAHs listed in Table 1 with different degrees of success. The result of analysis using PAIRS* to identify triphenylene is given as an example in Table 2. It is interesting to note that the strongest infrared absorption peak for triphenylene and for thiophene are positioned at 737 and 714 cm^{-1} respectively. Since PAIRS* interprets each spectrum based on peak locations, peak intensities, and peak widths, and since at this time we have not incorporated the interpretation tree for the PAHs the most probable functionality was interpreted as thiophene. The next two probabilities i.e., aromatic and aromatic 1,2-substituted seem reasonable conclusion for triphenylene. At the time of writing this manuscript we are in the process of writing and testing an interpretation tree for PAHs in the vapor state. It is hoped that this interpretation tree for PAHs can make the "functional group frequency" screening of PAHs possible.

REFERENCES

1. "The determination of Polynuclear Aromatic Hydrocarbon (PAHs) in ambient air by GC-FID". LSB routine approved method PAAPAH-AC8NCQ.1, Ontario Ministry of the Environment.
2. Nicolet/Aldrich vapor phase IR spectral library, June 1986.
3. Gurka D.F., Umana M., Pellizzari E.D., Moseley A. and de Haseth J.A., *Appl. Spectrosc.*, **39**, 297 (1985).
4. Gurka D.F., Titus R., Griffiths P.R., Henry D. and Giorgetti A., *Anal. Chem.*, **59**, 2362 (1987).
5. Gurka D.F. and Pyle S.M., *Environ. Sci. Technol.*, **22**, 963 (1988).
6. Shafer K.H., Cooke M., DeRoose F., Jakobsen R.J., Rosario O. and Mulik J.D., *Appl. Spectrosc.*, **35**, 469 (1981).
7. Gurka D.F., Hiatt M. and Titus R., *Anal. Chem.*, **56**, 1102 (1984).
8. Gurka D.F., Farnham I., Potter B.B., Pyle S., Titus R. and Duncan W., *Anal. Chem.*, **61**, 1584 (1989).
9. Mamantov G., Wehry E.L., Kemmerer R.R. and Hinton E.R., *Anal. Chem.*, **49**, 86 (1977).
10. Hinton, Jr. E.R., Mamantov G., Wehry E.L., *Anal. Letters*, **12**, 1347 (1979).
11. Childers J.W., Wilson N.K., and Barbour R.K., *Appl. Spectrosc.*, **43**, 1344 (1989).
12. Azarraga L.V. and Hanna D.A., "GIFTS, Athens GC/FT-IR Software User's Guide", U.S. EPA/ERL, Athens, GA, 1979.
13. Woodruff H.B. and Smith G.M., *Anal. Chem.*, **52**, 2321 (1980).
14. Yang M.J., Yang P.W. and Crawford G., "A personal computer program for the analysis of infrared spectra". Submitted to the journal of Computer Enhanced Spectroscopy (1990).

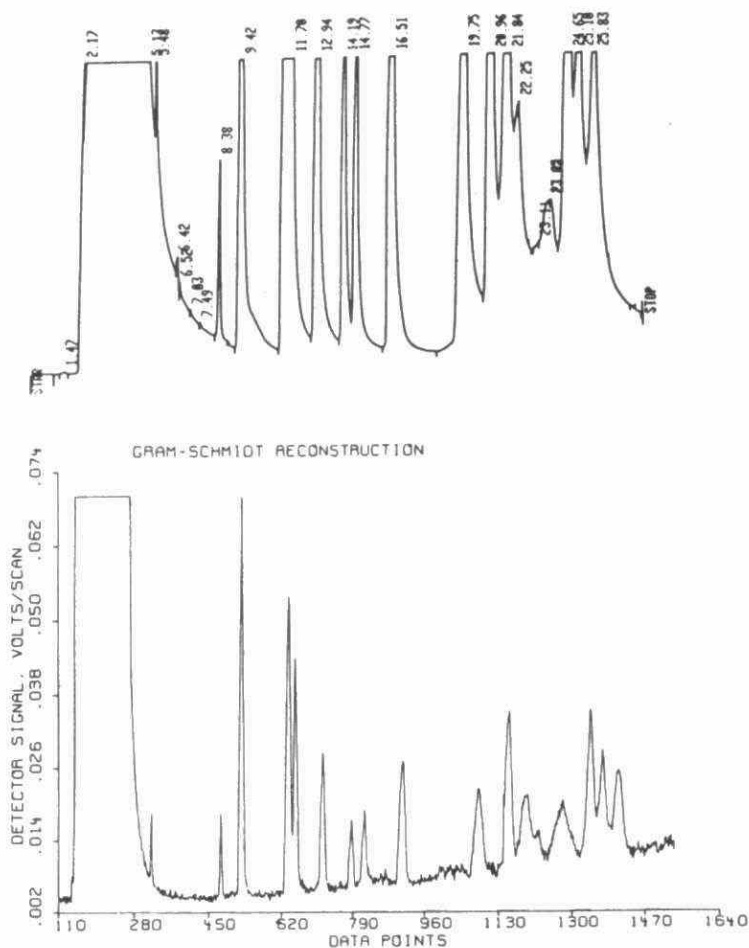


Figure 1- The gas chromatograph and the Gram-Schmidt reconstructed chromatograph from the analysis of a mixture of PAHs standard solution.

Table 1- The infrared absorption bands for PAHs in the spectral region 650 to 4000 cm⁻¹ (The peak with the highest intensity in each spectrum is underlined).

1)Naphthalene	<u>779</u> , 1006, 1507, 3065
2)2-Chloronaphthalene	739, 806, <u>849</u> , 880, 943, 1074 1137, 1192, 1232, 1345, 1454, 1593, 1628, 3066
3)Anthracene	<u>724</u> , 874, 1538, 3063
4)Phenanthrene	<u>730</u> , 806, 860, 1037, 1239, 1454 1500, 3065
5)2-Methyl anthracene	733, 1457, 1536, 1636, 2874, 2931 <u>3057</u>
6)9-Methyl anthracene	<u>726</u> , 773, 829, 996, 1306, 1346 1386, 1524, 1689, 2888, 3062, 3082
7)Fluorene	<u>736</u> , 1001, 1177, 1412, 1453, 1481 2916, 3028, 3071
8)Acenaphthylene	722, <u>770</u> , 829, 859, 1084, 1148 1387, 1421, 1461, 1619, 1804, 1918 2946, 3063, 3100
9)Acenaphthene	<u>782</u> , 834, 1366, 1427, 1607, 2854 2898, 2940, 3054
10)O-Terphenyl	<u>700</u> , 748, 1009, 1067, 1437, 1473 1597, 3031, 3069
11)M-Terphenyl	699, <u>749</u> , 796, 893, 1026, 1404 1447, 1474, 1497, 1594, 3036, 3069
12)P-Terphenyl	697, 751, 838, 1007, <u>1482</u> , 1525 1598, 3034
13)1-Methyl phenanthrene	<u>744</u> , 799, 876, 1461, 1599, 2881 2938, 2978, 3064
14)Fluoranthene	741, <u>773</u> , 825, 1426, 1454, 3066
15)Pyrene	708, 740, <u>837</u> , 1182, 1432, 1596 1786, 3051
16)Benzo[a]fluorene	715, <u>753</u> , 813, 1016, 1469, 2906 3066

...continued

Table 1 - Continued...

17)Benzo[b]fluorene	723, 1306, 3024,	766, 1415, <u>3064</u>	865, 1437,	953, 1473,	1017, 1503,	1188 2914
18)Triphenylene	<u>737</u> ,	1049,	1435,	1495,	3032,	3084
19)Chrysene	<u>756</u> , 3089	807,	858,	1030,	1424,	3066
20)Benzo[a]anthracene	<u>744</u> , 1500,	799, 1681,	880, 3062	1038,	1276,	1454
21)Benzo[c]phenanthrene	667, 1229,	<u>744</u> , 1417,	795, 1496,	832, 3014,	863, <u>3058</u>	1030
22)Benzo[b]fluoranthene	740, 1599,	774, 3071	887,	1442,	1454,	1524
23)Benzo[k]fluoranthene	740, 1446,	771, 1611,	821, <u>3063</u>	880,	1265,	1426
24)Benzo[a]pyrene	687, 1023,	741, 1079,	<u>757</u> , 1185,	821, 1263,	845, 3057	879
25)Benzo[e]pyrene	<u>744</u> ,	766,	826,	1440,	3056,	3086
26)Perylene	<u>767</u> ,	812,	1383,	1589,	3059,	3087
27)Indeno[1,2,3cd]pyrene	<u>730</u> ,	837,	879,	1381,	1443,	3057
28)Benzo[ghi]perylene	752,	768,	<u>841</u> ,	3055		
29)Dibenzo[a,c]anthracene	717, 3066,	<u>755</u> , 3077	877,	1432,	1493,	1508
30)Dibenzo[a,h]anthracene	739, 3077	<u>801</u> ,	881,	1023,	1088,	1454
31)9,10-Dimethyl anthracene	<u>743</u> ,	1367,	1389,	2941,	3088	
32)7,12-Dimethyl benz[a]anthracene	745,	805,	2934,	3073		
33)3-Methylcholanthrene	742, <u>2929</u> ,	799, 3049	869,	1503,	2866,	2893

Absorbance

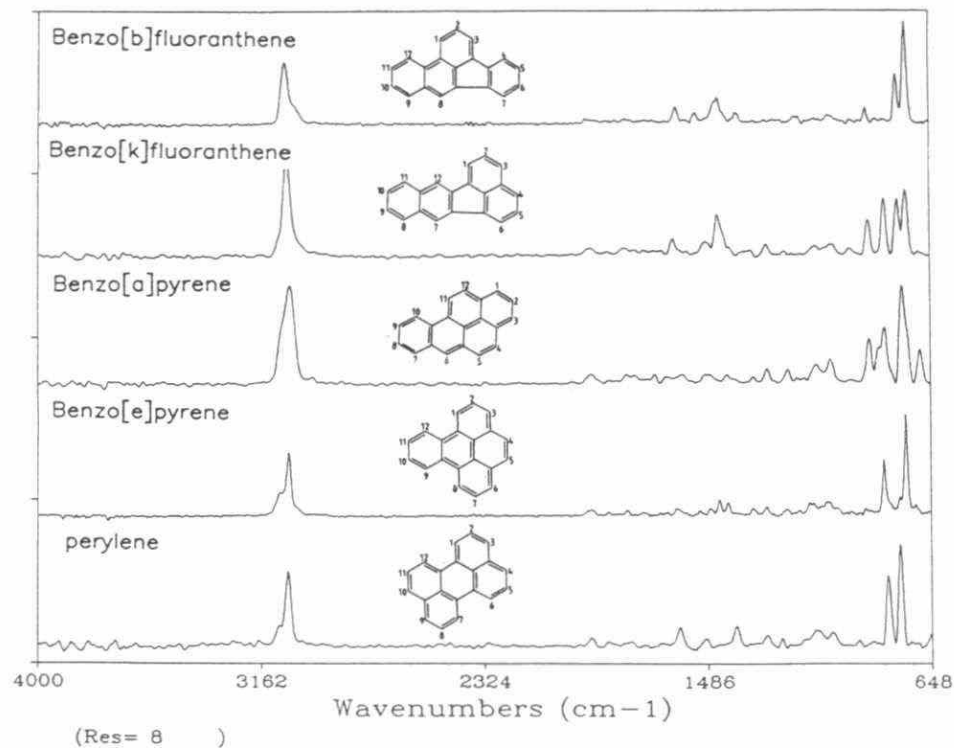


Figure 2- GC/FT-IR spectra for benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo [e]pyrene and perylene.

Table 2- The final report from PAIRS+ for triphenylene.

The final report from the upgraded PAIRS:

Spectral data summary for:

TRIPHENELYNE

The solvent is: neat

No empirical formula given

There are 6 peaks			
Line	Width	Intensity	Location
1	sharp	1	617
2	average	10	737
3	average	2	1435
4	average	1	1496
5	average	1	3032
6	average	3	3086

=====
Printout is sorted by probability:

	Group name	Probability
1)	THIOPHENE	0.60
2)	AROMATIC	0.55
3)	AROM-1.2-SUBST	0.55
4)	OLEFIN-(NON-AROM)	0.20
5)	OLEFIN-CH2=CR2	0.20
6)	OLEFIN-CHR=CR2	0.15
7)	OLEFIN-CHR=CHR(T)	0.15
8)	OLEFIN-CHR=CHR(C)	0.15
9)	OLEFIN-CHR=CH2	0.13
10)	FURAN	0.10
11)	AROM-MONOSUBST	0.06
12)	AROM-1.3-SUBST	0.06
13)	HETEROAROMATIC	0.06
14)	PYRIDYL	0.06
15)	PYRAZYL	0.06
16)	PYRIMIDYL	0.06
17)	PURINE	0.06
18)	INDOLE	0.06
19)	PYRROLE	0.01
20)	Z1	0.01

**The Struggle Towards Virtual Elimination of
Toxic Chemicals from the Environment**

F.W. Karasek Award Address

D. Mackay

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It appears that we are in the midst of a profound change in society's attitude towards contamination of the environment by chemicals. There is a growing public intolerance of the presence of even very low concentrations of chemicals in air, water, food and wildlife. Degraded environments are viewed with increasing disgust and anger. The concern is particularly strong in the Great Lakes Basin where the concept of "virtually eliminating" toxic chemicals from the environment has been warmly embraced by a receptive public. But there is difficulty defining what this means, how it is to be accomplished, and especially what concentration goals it represents.

Environmental scientists and managers, in industry, government and the academic world, while attempting to respond to these demands are also experiencing difficulty coping with "explosions" in (i) analytical capability to detect miniscule quantities of chemicals, (ii) the number of environmental media which must now be analysed and assessed, (iii) the number of candidate chemicals of concern, (iv) data on these chemicals' subtle toxicology and (v) in regulations pertaining to chemical use exposure and discharges.

Environmental science technology and regulation are lagging behind public and hence political demands, forcing decisions to be made in the absence of adequate knowledge. There is thus a compelling incentive to undertake more well-directed research in the hope that it will lead us to a better understanding of the sources, fate and effects of chemicals in the environment, and to effective and economic controls which will satisfy the public's increasing demands.

Although much remains to be done we should acknowledge that the 1970s and 1980s have seen the emergence of a formidable body of knowledge concerning the number and nature of chemical contaminants, and their physical-chemical, biological and toxicological properties. We have a remarkable, and still increasing, capability of detecting the presence of chemicals at very low concentrations in all compartments of our ecosystem. We now know that chemicals behave in a generally predictable way, migrating throughout the various media of the environment, and often concentrating to remarkably high levels in particular locations such as animal lipids and aerosols. It should now be possible to avoid repeating past mistakes such as the excessive releases of DDT, PCBs and mercury. To guarantee this we need an improved capability of assessing environmental fate and toxicity of chemicals.

A system appears to be evolving in which certain chemicals such as PCBs will be totally banned from commerce; others such as lead or mercury will be used, but in limited quantities and under strictly controlled conditions of compulsory recycle or disposal; and the remaining relatively benign chemicals which remain in general use will be discharged

to the environment only in known, small, acceptable quantities after state-of-the-art or "best available" treatment and with a full assurance that their fate and effects are well understood. It will be no longer acceptable to discharge chemicals indiscriminately, surreptitiously, or in large quantities, especially when there is suspicion of any effect on ecosystems or on human health. A view is emerging that the best guarantee of human health is not to shield ourselves from contamination but to work towards creating a healthy contaminant-free ecosystem in which the most sensitive wildlife species thrive. Essentially, society will manage all chemicals from cradle to grave with special attention to those which are most toxic and persistent.

It is suggested that the current of changing public attitude of demands for a high quality ecosystem, and assurance of unimpaired human health is taking us in this direction. Assurances that chemical concentrations and exposures are low and will probably not produce adverse effects are increasingly falling on deaf, unreceptive ears. There is a growing demand for simple elimination of chemicals from the outdoor and indoor environments, and the workplace, regardless of the chemicals' nature, concentration or toxicity. This creates a considerable challenge for the community of environmental scientists and managers whose task it is to respond to these demands with a full awareness of the current state of the art, economically, professionally and with sensitivity.

GRAPHICAL TECHNIQUES FOR THE PRESENTATION OF INTERLABORATORY STUDY DATA - A DIAGNOSTIC AID

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ABSTRACT

Historically, most interlaboratory studies have documented current performance and evaluated the performance against a standard in tabular form. Graphical techniques of evaluation provide for a more immediate comparison of performance and a greater incentive for participants to improve their performance. Examples from a series of interlaboratory studies co-ordinated by Laboratory Services Branch of Environment Ontario during 1988-90 demonstrated this approach.

INTRODUCTION

The role of the interlaboratory or collaborative study to establish the precision of an analytical procedure is well established. The American Society for Testing and Materials (ASTM) and the Association of Official Analytical Chemists (AOAC) have published guidelines for conducting this type of study (1, 2). The data is treated and summarized using classical statistical techniques and an accepted standard of performance is established.

Interlaboratory performance studies are then used as a means of monitoring the ongoing performance of a group of analytical laboratories that are testing environmental samples. These studies have three functions: documentation of current performance, evaluation of that performance against a standard, and inducement to improve both individual and group laboratory performance

(3). There are many examples in the literature of interlaboratory performance studies that tabulate current performance and evaluate the performance against a standard using classical statistical techniques. Less frequently are the interlaboratory studies used to focus on ways to improve an individual laboratory's performance.

MOE LABORATORY SERVICES BRANCH APPROACH

The Laboratory Services Branch (LSB) of Environment Ontario initiated a series of Interlaboratory Performance Management Studies in 1988 in support of the ministry's Municipal and Industrial Strategy for Abatement (MISA) Program. The studies were designed not only to document the current level of performance of laboratories capable of performing MISA analyses, but also to be used as a tool for improving an individual laboratory's performance. Each study focused on a specific MISA analytical test group or groups (4), with different tests being repeated over time so as to monitor improvements in performance.

The traditional approach of reporting interlaboratory means, medians, and standard deviations for the various parameters has been included for the LSB studies, as they provide a familiar form of comparison for the participants. However the assessment of each individual laboratory's performance, and the recommendations for improvement are based on different graphical techniques.

The Youden two-sample plot (2) is a well-established technique for assessing intralaboratory precision. Traditionally it has been applied to single-parameter tests. The standard deviation of the results can be used to calculate a limit for acceptable performance, with outlying laboratories flagged (Figure 1). This approach works effectively for most conventional and inorganic analyses.

By applying the Youden two sample technique to the results from an organic gas chromatographic (GC) scan, the interanalyte repeatability and bias may be assessed for an individual laboratory (Figure 3). Tolerance limits may be assigned or calculated, to rank the precision and the bias of the data set. Outlying parameters may be flagged, as opposed to flagging an outlying laboratory.

To assess a laboratory's performance across a GC scan, the results from a sample may be converted to percent recovery of the design value, arranged in elution order, and presented as a bar graph (Figure 5). Trends across the scan may be noted, with recommendations for improvement. This may include patterns of increasing or decreasing recovery, suggesting adjustments for the GC temperature programming. A specific group of parameters within the scan may be over- or under-recovered, suggesting problems with extraction efficiency. Individual problem parameters are easily identified, and steps can be taken to check calibration standards or the

appropriateness of the method for a specific parameter.

The following examples from several different LSB Interlaboratory Studies demonstrate how these graphical techniques may be used as a diagnostic aid to help improve laboratory performance.

EXAMPLES

Interlaboratory Study 89-6: Metals and Hydrides

Interlaboratory Study 89-6 was conducted in September 1989 to assess the interlaboratory variability for the analysis of metals and hydrides in spiked reagent water. A total of 36 laboratories participated in this study (5).

The traditional Youden two-sample plot was used to assess the results from this study (Figures 1 and 2). To evaluate the results and determine outliers, a pooled standard deviation of the two spiked samples was calculated (5). This acceptance criteria is indicated by the circle on each plot and outlying laboratories are flagged. The location of the outlying results in either the upper right or lower left quadrants, demonstrates either a systemic high or low bias, usually associated with a difference in calibration standards.

Interlaboratory Study 89-5: Acid and Base/Neutral Extractables

Interlaboratory Study 89-5 was conducted in May 1989 to assess the interlaboratory variability for the analysis of acid and base/neutral extractables in spiked reagent water. A total of 15 laboratories participated in this study (6).

The Youden two-sample technique was applied to the results across the GC scan after converting the results to percent recovery of the design value. Tolerance limits of $\pm 20\%$ for performance were assigned (Figures 3 and 4). Interanalyte repeatability can be deemed acceptable if all the data pairs fall within the tolerance limits, as demonstrated in Figure 3. Biases within the scan can be easily recognized as demonstrated in Figure 4.

Interlaboratory Study 89-1: Volatile Organics

Interlaboratory Study 89-1 was conducted in January 1989 to assess the interlaboratory variability for the analysis of volatile organics in spiked reagent water. A total of 16 laboratories participated in this study (7).

To assess the performance across the GC scan, the results were converted to percent recovery of the design value, arranged in approximate order of elution, and plotted as a bar graph (Figure 5). The results demonstrate various patterns of performance. Laboratory 1007 demonstrates a pattern of increasing recovery across the scan, suggesting that the temperature

program may initially be too high, resulting in volatilization of the target parameters. Parameters that are over-recovered are readily identified, suggesting that the calibration standard should be cross-checked for accuracy. The results for Laboratory 1014 indicate a subset of parameters that demonstrate a pattern of decreasing recovery across the scan. This may indicate that the method used by this laboratory is not appropriate for the analysis of these parameters.

CONCLUSION

Graphical presentation of interlaboratory data can facilitate interpretation, and reveal patterns that are not detected by tabular or statistical summaries. They provide a fresh perspective and insights into relationships which may otherwise be overlooked or missed, providing greater incentive to improve laboratory performance.

REFERENCES

1. *Annual Book of ASTM Standards*, Vol. 14.02. "E 691-87 Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method". 1990. American Society for Testing and Materials. ISBN 0-8031-1568-7.
2. Youden, W.J. and Steiner, E.H. *Statistical Manual of the Association of Official Analytical Chemists*. 1975. Association of Official Analytical Chemists. ISBN 0-935584-15-3.
3. Cussion, S. and King, D.E. "Organics Laboratory Performance Management by Interlaboratory Comparison". *Proceedings from Dioxin '90 Conference*. 1990. In Press.
4. ONTARIO REGULATION 695/88 as amended to Ontario Regulation 533/89 under the Environmental Protection Act; Effluent Monitoring - General.
5. *Interlaboratory Study 89-6: Trace Metals, Hydrides, Total Phosphorus, Total Kjeldahl Nitrogen, and Phenols by the 4AAP Method in Reagent Water*. 1990. Draft.
6. *Interlaboratory Study 89-5: Extractable Organic Parameters in Reagent Water*. 1990. Draft.
7. *Interlaboratory Study 89-1: Volatile Organic Parameters in Reagent Water and Oil and Grease in Reagent Water and Effluent*. July 1990. Queen's Printer for Ontario. ISBN 0-7729-7164-1.

FIGURE 1

FIGURE 2 :INTERLABORATORY STUDY 89-6

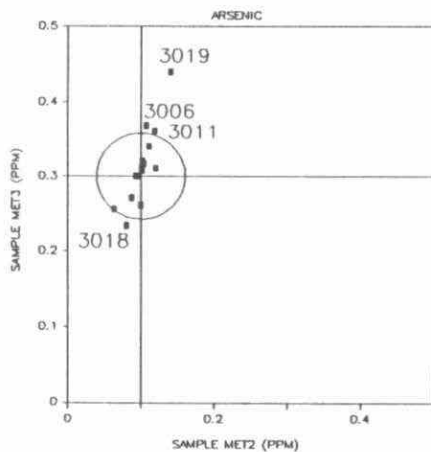


FIGURE 2

FIGURE 12:INTERLABORATORY STUDY 89-6

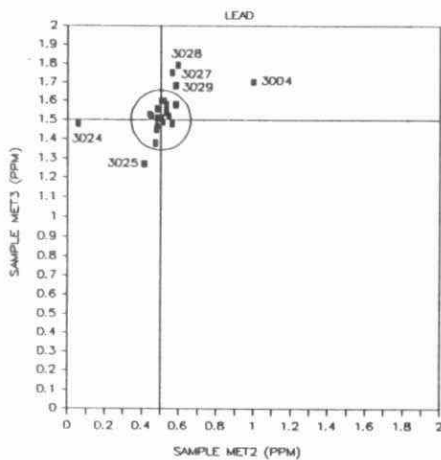


FIGURE 3

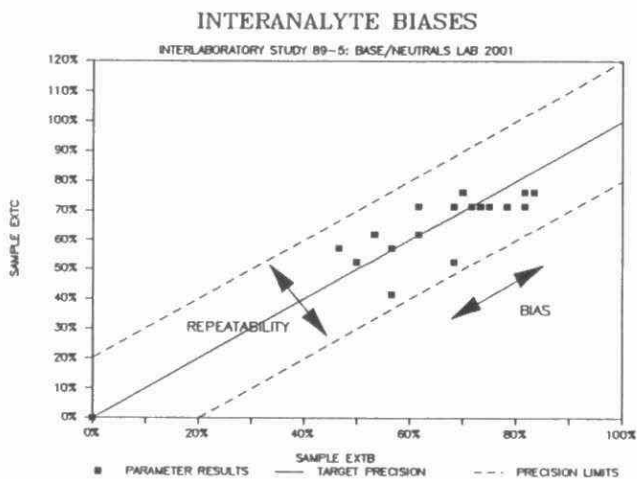


FIGURE 4

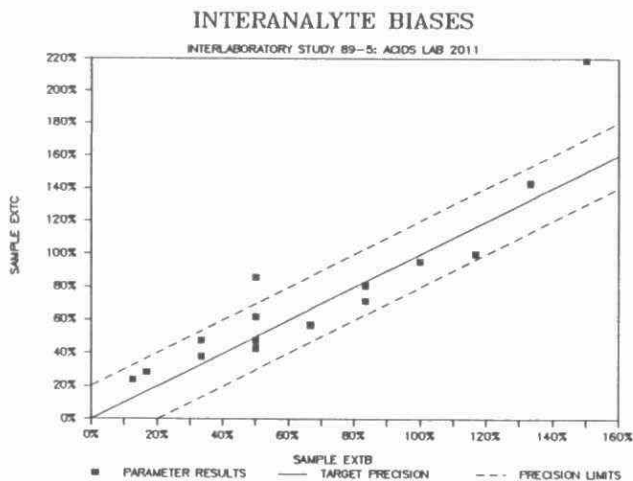
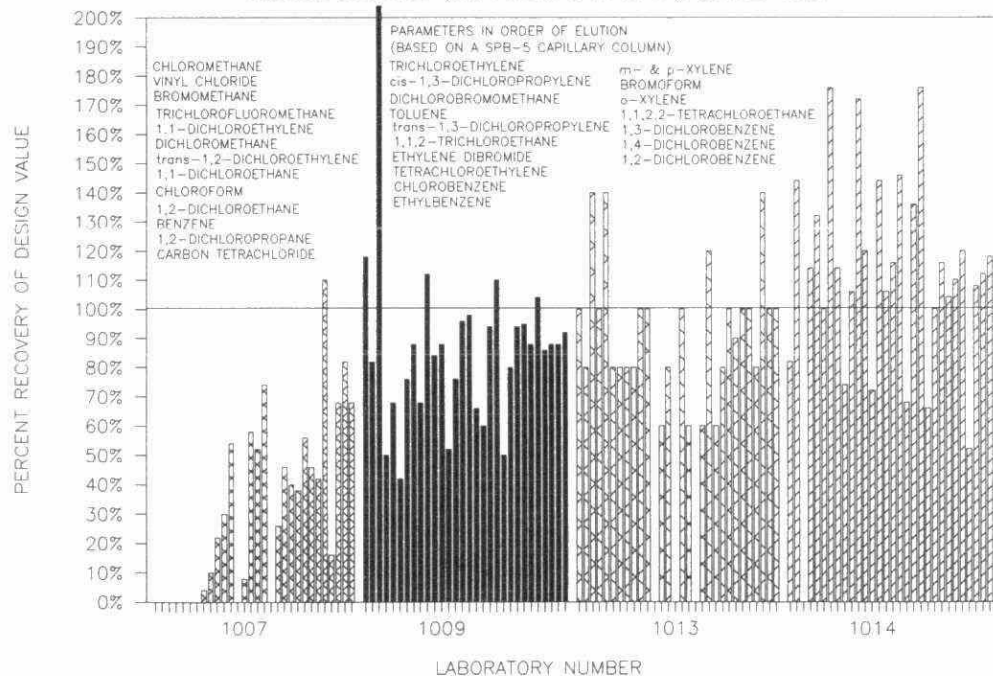


FIGURE 5

FIG. 3 - INTERLABORATORY STUDY 89-1

VOLATILE ORGANICS (MISA GROUPS 16 & 17); SAMPLE VOLB



Design, Constraints and Implementation of Rules Within ACexpert.

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Abstract The full value of expert systems in solving analytical chemistry problems can only be realized when the technical methods used to create these complicated programs are understood by analytical chemists. While the knowledge base, inference engine and user interface needed in each expert system can be written in either a procedural language (such as C or FORTRAN), or in a specially developed language like LISP or Prolog, the expert system shell appears at this time to offer the most reliable and productive route for the analytical chemist to follow. Expert system shells provide a programming environment that primarily offers built in subsystems that can acquire facts and rules and operate the inference engine. In this paper, we describe the continuing development of the expert system, **ACexpert**, a program which will control all aspects of metal ion determination carried out by atomic absorption spectrometry. Our present work involves coding analytical method and diagnostic rules for use with the analytical methods selection module **ACmethods** and the quality control module **ACdiagnostic**.

Introduction

Expert system programs offer the analytical chemist several distinct tools for use in the laboratory. At the present time, it is possible that their most important value is in providing rapid access to chemical information that has been verified for highly specific tasks, and that is presented to the user in a highly organized manner. This view of the role of an expert system readily leads to the use of expert system programs as advisors for methods development and for analytical problem solving. Prior to the introduction of expert system shells, the development of expert system software required a considerable investment in both money and time. With the advent of the expert system shell, the knowledge engineer, expert, and programmer may be one and the same person. As the capabilities of these expert system shells become better known to analytical chemists, we expect that these software packages will become as important as the procedural programming languages of FORTRAN, BASIC, Pascal, and C are today. Excellent examples of the application of expert system techniques within analytical chemistry may be found in two books edited by Pierce and Hohne^{1,2}, and we have discussed the results of earlier work on ACexpert previously³⁻⁶.

Analytical chemists can use the expert system's capability to manipulate symbolic data to carry out many of the tasks currently completed with procedural programs, however, now the program can be coded to check that the results obtained by the calculation are reasonable. This type of program can be designed to operate instruments, which may be considered to be a 'black box' by their operators, 'intelligently'. We have considered^{3,4} that instruments that fall under this class are atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), high performance liquid chromatography (HPLC), and gas chromatography-mass spectroscopy (GC-MS).

ACExpert has been designed to carry out completely automated metal concentration determination by atomic absorption spectrometry. Solutions of samples, blanks, modifiers and standards will be prepared by an automated liquid sample handling station, and then pumped into the flame of an atomic absorption spectrometer. This environment is well suited to test rule-based methods selection and quality assurance modules, as well as the incorporation of modules to access analytical information stored on different databases. Overall, **ACExpert** will act as an advisor and assistant to the analytical chemist in completing analyses.

Expert systems applications within the field of analytical chemistry¹⁻¹¹ fall into two broad categories: (i) systems that are developed to interpret experimental results, and (ii) systems that provide guidance as to the course of action the analyst should take. The challenge in the development of an expert system is to produce a system that will dispense chemical advice at or near the level of a skilled chemist, while at the same time being capable of recognizing that both the skilled chemist and the computer expert system may at times make mistakes. The development of an expert system, must start with some concept of what an "expert" is, how experts perform scientific tasks, and how scientific "expertise" is acquired. There are two main characteristics that distinguish experts from novices. (i) Experts are usually expert only with respect to a narrow area of expertise, and (ii) they rely on shortcuts that they have distilled from their previous experience¹². As a consequence, experts tend to rely more on pattern recognition and memory at the expense of deductive reasoning, than do novices^{12,13}. We have found during our work that a major limitation in the use of a rule-based program is the complexity of the user interface. We find that expert users of the system are more comfortable when the questions and solutions are offered in a style that is equivalent to their knowledge in the field. This means that the user interface must allow information transfer between the expert and program to be as efficient as possible. In order to meet this challenge we are currently exploring the possibility of using Windows 3.0 (Microsoft) as well as using graphical images in place of textual statements of chemical or analytical status.

Structure of an Expert System

Expert systems consist of three important modular components: the user interface, the inference structure, and the domain knowledge or expertise, as shown in Figure 1. The arrows represent the formal exchange of information between each of these distinct subsections of the expert system. With the appropriate shell, the analytical chemist can customize these subsections to produce an expert system that will provide a new generation of programming assistance for solving chemical problems.



Figure 1. The Structure of an Expert System. The double headed arrows illustrate how information is exchanged between the three different modules of the program. It is important to the implementation of an expert system that there are no direct links between the user interface and the knowledge base. This allows the knowledge base to be changed after the program has been written.

Development environments for expert systems are known as shells. These shells are expert systems that generally contain an inference engine, and various interface and knowledge acquisition aids, but lack rules and facts in the knowledge base. We illustrate the structure of an expert system shell and its components in Figure 2. The use of these shells greatly simplifies the development of an expert system.

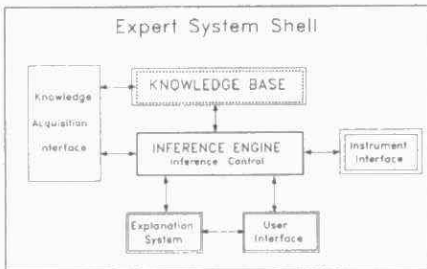


Figure 2. Structure of an Expert System Shell. Compared with an expert system language, the expert system shell includes an empty, 'shell', knowledge base and a knowledge acquisition module. In most simple expert systems the possibilities for modification of the explanation system and the user interface are limited. However, specialized interfaces such as an instrument interface can be added.

Inference engine The inference process involves asserting the conditions under which facts are true for certain knowledge or likely to be true for uncertain knowledge. Three inference strategies are commonly used: forward-chaining, backward-chaining, and the rule-valued method¹². These inference strategies can be combined with either a depth-first or a breadth-first search strategy¹². The depth-first search strategy, Figure 3, requires an affirmative search through all levels of a branch of the tree, until a contradiction or conclusion is reached. The breadth-first search strategy requires that each level of all the branches be searched before a conclusion is reached. In forward-chaining, the inference engine uses the user's information to move upwards through a tree of rules towards a single conclusion. In backward-chaining, the system starts with a conclusion (this could be an

analytical method) and requests from the user data to confirm or contradict this conclusion (these data could be the matrix, element, solvent, concentration range, regulatory agency, etc.).

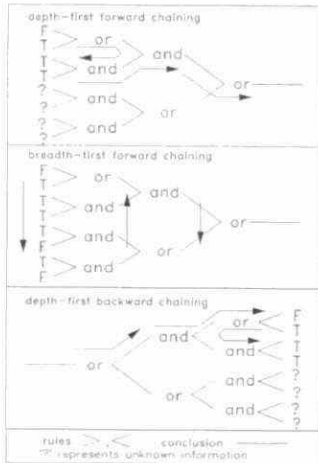


Figure 3. Different logic strategies used by inference engines: Forward Chaining with a Breadth-First Search, Forward Chaining with a Depth-First Search, and Backward Chaining with a Depth-First Search. The arrows indicate a search path that may be followed through the tree of rules and clauses to arrive at a conclusion.

Knowledge base The knowledge base holds information in terms of data, as well as rules that link these data together. The information may be stored in the program itself or the knowledge base may be stored as a separate database. The developer's job is to acquire the necessary information for the knowledge base. This information will be a combination of personal experience of experts as well as published data.

Interface One of the most important aspects of the expert system is the implementation of the user interface. A good match between the system and the user is vital. The user interface has to handle all communication between the user and the expert system in a way that maximizes the flow of information. The expert system must be able to explain the reasoning behind its conclusions. An explanation subsystem is usually set up for this purpose. The knowledge engineer can also use this system to elaborate on the advice that is given to the user. Often, however, the explanation displayed simply takes the form of an exact textual copy of the rules that were used to provide the advice, so may not be at all helpful to anyone but another expert and certainly of no use to the novice user.

Comparison between Conventional and Expert System Programming

In the expert system, the separation of the knowledge base from the inference engine and the user interface, allows for modular expansion and easy maintenance of the knowledge base. In conventional procedural programs, the domain knowledge of facts

and rules is completely integrated into the inference structure. This means that the developer must classify all of the objects and define all of the relationships and concepts that are to be used in the program before any code is written. Procedures are then created that will infer new instances of relationships from existing ones, in a sequential fashion. Like the execution of the program, the program is developed in a sequential fashion. The result of this integration is unwieldy development and practical limitations to the complexity and size of the system that can be produced.

By way of contrast, the development of an expert system is more circular and evolutionary. Often the detailed specifications of the program, and what it is to accomplish, are not well defined in advance. The relationships and concepts that are required to complete the logic of the expert system are discovered by the knowledge engineer and the expert during the development of the system prototype. In addition, expert system techniques typically attempt to separate the control structure from the domain knowledge. During the prototype stage of development, rules in the knowledge base may be easily changed or added in order to fine tune the reasoning.

One of the overwhelming features of chemical knowledge is that information, procedures, and techniques are always evolving. The amount and complexity of that knowledge is always increasing. The structure of a conventional programming environment, although efficient for repetitious rigidly defined tasks, is incompatible with the dynamic nature of developing chemical knowledge and systems that dispense advice. Expert system shells, which provide the chemist with a complete programming environment, relieve the expert of the task of creating the user environment. The chemist can focus on the problem at hand which is the incorporation of his or her expertise into a program that will dispense advice by tailoring the shell to produce the working expert system.

ACexpert

Metal concentration determination using AAS requires the completion of several tasks, each of which require extensive knowledge and expertise. With the increased automation of modern instrumentation and the demands for increased efficiency and volume of analyses, the organization, operation and control of these complex tasks are well suited to the use of an expert system. Although the decisions about chemical analyses are complex, the procedures and methodologies of analytical expertise are well understood. For this problem the three most important criteria for the successful development of an expert system are fulfilled: (i) this is a significant problem for which there is a demand for a solution, (ii) acceptable expert system development tools are available, and (iii) the expertise which will be used to create the expert system is readily available from a variety of sources.

In an analytical laboratory, there are several steps that always take place between receipt of a sample and dispatch of the report. Typically, the manager consults with both the customer and the regulatory agency to determine the method that is to be used. The quality control and quality assurance programs and the report writing are carried out as

separate tasks by the manager and the analyst. In terms of analysis by AAS, sample preparation is followed by determination of the concentration of metal by empirical comparison with a calibration curve for that analyte. QA/QC programs check the precision, accuracy and stability of the instrument over both the short and long term. Matrix effects, physical interferences, and spectral interferences are among the analyst's expert knowledge. Although incorporation of an expert system into the analytical laboratory will change how some of these tasks are carried out, the judgement and expertise of an analytical chemist or a skilled technician will still be needed to interpret the information offered by the computer system. We list in Table 1 specifications that we believe are necessary for an expert system that operates in an advisory or consultative role (see Table 2) within an analytical chemistry laboratory.

There are four steps that must be completed in the development of an expert system program:

- (i) Problem determination and specification stage.
- (ii) Development of the initial demonstration prototype.
- (iii) Development of the expanded prototype.
- (iv) Completion of the deliverable system.

In our work to date, we have completed (i)³⁻⁶, and are completing (ii), while exploring the technical difficulties involved in scaling up to (iii).

The problem determination and specification stage, requires the completion of a detailed description of the concepts, and the identification of criteria and case studies that will be used to produce a small version of the expert system in order to demonstrate its overall feasibility.

Table 1. Specifications for an expert system in an advisory role.

1.	the system should be built around a powerful user interface
2.	the system should be able to use the user interface to determine the conditions to be satisfied in an order of priority (analyte, regulatory body, analytical technique, sample type, etc.), and allow the user to determine the effect of a specific choice on the advice provided by the system.
3.	the system should have the ability to use generic rules that govern the measurement of analytical data as well as using specific methods stored on a database.
4.	the system should be able to use ambiguous information and also be able to offer multiple answers with some form of ranking, when necessary.
5.	the system should be able to access information stored by traditional database and spreadsheet programs.
6.	the system should be able to explain the reason for using the procedures suggested.
7.	the system should be able to integrate its decision making with other expert systems.

ACexpert encompasses the complete system that will be used to carry out completely automated metal concentration determination. The structure is described as a set of expert systems shown in Figure 4. Each expert system will perform a separate task and each will be capable of acting independently or as a module of the full system. In this scheme, the analyst's role fundamentally changes from one of a technician to that of a supervisor of the expert system, **ACanalyst**. However, the manager's role remains the same, although he or she now has the assistance of both the analyst and **ACexpert** in order to monitor the completion of analyses. **ACassurance** is the quality assurance expert system that will be used by the manager and the analyst to assist in the execution of a laboratory quality assurance program. Incorporated in this expert system are modules that will be used to provide instruction and advice to the laboratory personnel in carrying out their tasks and completing the analysis procedures thoroughly. **ACanalyst**, the quality control and process control expert system, comprises five separate expert systems that will be used in methods selection, process control, analysis, fault diagnosis, and quality control. The functions of the individual expert systems have been outlined previously³⁻⁶.

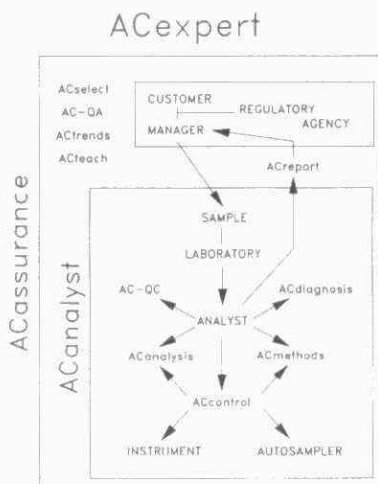


Figure 4. **ACexpert** is a chemical analysis expert system which provides interactive assistance to the analyst. The flow of information or the movement of the sample is illustrated by the connecting lines.

In normal operation, the analyst would manually confirm the method selected by **ACmethods** and monitor the performance of the analyses. All other aspects of the analysis would be carried out automatically, although still under the direct supervision of the analyst.

The implementation of a demonstration prototype of each of the separate expert system applications is next step. Each task that the expert system is expected to complete may require a separate inference and knowledge base structure. The specifications for these structures may vary considerably depending on the task that it is to perform. For example, the structure of a consultative expert, will differ considerably from that of a real-time monitoring and control expert or an interpretive expert system. A summary of the types of expert systems, which might be useful to the analytical chemist is provided in Table 2.

At a minimum, a shell must have a knowledge representation scheme, an inference or search mechanism, a means of describing the problem, and a way to determine the status of a problem while it is being solved. Consultative or diagnosis experts, may be used for methods selection or fault finding (**ACmethods**, **ACdiagnosis**), and typically are built with rule-based shells that require consistent relationships between causes and symptoms, or conditions and conclusions, as well as the ability to identify these relationships. The decision making is made more difficult if symptoms are masked by other symptoms, the symptoms are intermittent, the data is inaccessible, or if there is uncertainty and lack of knowledge about the relationships between the causes and symptoms.

Table 2. Descriptions of specific types of expert system and examples of their use in the analytical laboratory.⁸

Type	Use
Consultation	Selecting a method from a list of ingredients or procedures; ACmethods , ACtrends
Control	Directing the overall operation of an instrument or process control system; ACcontrol
Diagnosis	Determining probable causes of malfunctions or incorrect data values from observables; ACdiagnosis
Instruction	Training operators and technicians through simulations and question and answer sessions; ACteach
Prediction and simulation	Inferring probable consequences from a given situation; ACteach , ACanalysis , ACtrends

Use of the KDS3 Expert System Shell

The KDS environment for expert system development, provides the developer with substantially the same interface and performance characteristics as the end product that the user will encounter. This shell, like many other inductive shells, generates rules from examples. The developer enters a large number of examples for the machine's information base into the development system. The development system then uses an algorithm to convert the examples into a rule or number of rules and to determine the order that the system will follow when questioning the user and making a recommendation. Unlike other production, rule-based systems, KDS does not deal with attributes or values, but only with conditions, which are input into KDS as text strings that are either true, false, or known with some degree of certainty¹³. To KDS, every entry is simply a string of text that has some factors associated with it and a certain place in the logical hierarchy (see the paper in this volume by S. Lahiri, Q. Zhu and M. J. Stillman, that describes in more detail the relationship between conditions and conclusions).

The KDS compiled expert system uses the knowledge of the conditions and rules that make up the knowledge base to ask questions of the user in the most efficient manner according to the number of times a condition has been used to arrive at a conclusion. For example, the KDS system will request validation of a condition that has been used by 4 conclusions before a condition that has been used by only 2 conclusions. However, as a consequence of the KDS inference strategy, which selects the ordering of the question, the questions may be asked in an unusual order for someone who is expecting a hierarchy relationship between the questions. For example, when the system begins to determine the information summarized in Table 3, the questions asked may not follow the route that we have used. Instead conditions that might be considered out-of-order are asked first.

The KDS expert system shell carries out its own testing and validation of the logic provided by first the developer, and then the user. During development, the KDS shell ensures that the logic connecting conditions does not change as more information is encoded; during use, the shell checks that answers provided by the user do not conflict with the logic originally given by the developer.

An inductive shell, such as KDS, provides an excellent prototype environment that has extensive interfacing capability to other systems and procedural programs in order to input information through a variety of special interfaces. The rigorous logic, which the developer must follow in order to create a usable expert system, results in well implemented system that can be used as a learning experience for the developer as well as the user. As indicated in the section on Experts and Expertise, it is often difficult for experts to report how a solution was arrived at. The "step by step", example-driven programming of an inductive shell, like KDS, provides an excellent environment for resolving the ambiguity of unclear rationalizations.

The **ACmethods** is based on data given in the Varian Canada applications manual for metal determination in aqueous samples. The prototype advice is presented to the user as simple text. As the expert system evolves, we will tailor the **ACmethods** manual to the needs of the local laboratory by incorporating access to methods stored as entries in a database. The first prototype of **ACmethods** uses a small set of attributes or conditions (analyte, regulatory body, analytical technique, sample type, sample preparation method, or detection limit) to determine the method to suggest to the user. As the **ACmethods** expert system grows in complexity this set of attributes will need to be expanded.

Implementation of ACmethods

The knowledge base for **ACmethods** was implemented with the KDS3 development system.

Table 3. User-provided information to be transferred from the user interface to **ACmethods** in order for a method to be selected.

	Control information for ACmethods	Choices available
1.	Analytical technique to be used	Atomic absorption spectrometry.. flame, vapour phase, graphite furnace (AAS) Inductively-coupled plasma atomic emission spectrometry (ICP-AES) gas chromatography (GC) liquid chromatography (LC) ion chromatography (IC) GC-MS
2.	Element to be analyzed for	Periodic Table appropriate for technique
3.	Known interfering elements	Periodic Table or Dictionary appropriate for technique
4.	Matrix for sample	Natural waters Sediments Organic material Effluent
5.	Chemical properties of the analyte	Mineral acid-extractable metal Metal in suspended material of sample Metal can be extracted with organic solvent to eliminate interferences
6.	Regulatory agency	Ministry of the Environment, Ontario Water Quality Branch of Environment Canada in Ottawa

In this example, the expert system presents the user with both menus and individual questions during the course of the session in order to select the appropriate method. In a more complex expert system the KDS standard interface could have been replaced with a customized user interface or an instrument interface, if real-time data input and analysis were desired.

Discussion

Success in the development of a new expert system is strongly dependent on the planning stages which must include a significant component of system validation and evolution. The challenge for the chemist will be to become knowledgeable about the available expert system shells that can be used in the development of prototypes. As the degree of complexity increases, so the developer will have to begin to use tools that are more sophisticated in order to handle decision making. These tools will include frames, objects, and blackboards. However, like any programming environment, shells that incorporate the more sophisticated knowledge representation strategies will make greater demands on the programming skills of the knowledge engineer.

Several modules in **ACexpert**, such as **ACmethods**, **ACselect**, **ACTrends**, and **ACteach**, will require extensive access to a database in order to supplement the complex rules and facts that will be needed to provide advice from more involved or ambiguous information. For such systems an expert system shell that organizes knowledge as objects or in frames will be required.

Acknowledgments

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References

1. "Artificial Intelligence Applications in Chemistry", T. H. Pierce, and B. A. Hohne, eds., American Chemical Society, Washington, 1986, ACS Symposium Series 306.
2. "Expert System Applications in Chemistry", B. A. Hohne and T. H. Pierce, eds., American Chemical Society, Washington, 1989, ACS Symposium Series 408.
3. W. R. Browett and M. J. Stillman, *Progress in Analytical Spectroscopy*, **12**, 73-110 (1989).
4. W. R. Browett and M. J. Stillman, in "Expert System Applications in Chemistry", B. A. Hohne and T. H. Pierce, eds., American Chemical Society, Washington, 1989, ACS Symposium Series 408, pp 210-235.
5. M. J. Stillman, M. Moussa and Z. Gasyna, MOE Technology Transfer Conference, Volume II, Analytical Methods, 254-261 (1989)
6. M. J. Stillman, T. Cox and W. R. Browett, MOE Technology Transfer Conference, Session D, Analytical Methods, 195-228 (1988)
7. T. P. Bridge, M.H. Williams, and A. F. Fell, *Chem. Brit.*, **23**, 1085 (1987).

8. F. A. Settle, Jr., M. Pleva, C. Booker, H. Iams, D. McClintock, and T. Moore, Amer. Lab., **March**, 17 (1987).
9. V. Berry, Amer. Lab., **April**, 126 (1987).
10. K. Parsaye, and M. Chignell, "Expert Systems for Experts", John Wiley and Sons Ltd., New York, 1988.
11. P. E. Slatter, "Building Expert Systems: Cognitive Emulation", Ellis Horwood Ltd., West Sussex, England, 1987.
12. H. Schildt, "Artificial Intelligence Using C", Osborne McGraw-Hill, Berkeley, CA, 1987.
13. E. R. Tello, "Mastering AI Tools and Techniques", Howard W. Sams & Cmpy. Indianapolis, USA, 1988.

Glossary

- Backward Chaining:** An inference control strategy that regulates the order in which inferences are drawn. In a rule-based system, backward chaining is initiated by a goal. The system attempts to prove the specified goal by determining the truth of the clauses that become secondary goals.
- Breadth-first Searching:** A search strategy in which all rules at the same level of a particular hierarchy are pursued before moving to the next level.
- Conventional (procedural) language:** A language in which an algorithm for solving a problem is expressed in an objective form and can be used repeatedly to solve a variety of problems that can be addressed by the same algorithm.
- Depth-first Search:** A search strategy in which all levels of a specific conclusion are pursued as deeply as possible until that conclusion is proven true or false. The system searches down a single branch of a tree until it reaches the end. It then backs up to the first unsearched branch and goes down that branch, and so on.
- Domain:** A subject matter area or problem-solving task.
- Expertise:** Skill, knowledge, rules, and procedures in a particular domain. These characteristics imply not only knowledge of the domain, but also the ability to organize this knowledge into chunks and networks for practical use.
- Expert system shell:** A very high-level expert system language that permits the construction of very powerful systems with a minimum of programming.
- Explanation System:** That part of an expert system that permits the user to query about the reasoning process used in reaching a particular goal state.
- Forward-chaining:** A type of reasoning strategy that begins with the known facts and works forward, trying to find a goal for which all of the facts are true.
- Frame representation:** A type of knowledge representation in which an object is associated with a number of attributes or properties, and the attributes are associated with values. The object is represented by a frame, the attributes by slots in the frame, and the values are stored in the slots.
- Hierarchy:** An ordered network in which some objects are subordinate to others. Hierarchies imply inheritance. Objects at the higher level are the parent, and objects immediately subordinate are the children.
- Induction system:** (or Example-driven system) A knowledge system that generates a decision tree or rules from a set of examples.
- Inference engine:** That part of an expert system that infers new facts from existing facts using rules in the knowledge base, and also control the order of inference.
- Knowledge:** Facts and relationships about a particular domain that can be used to solve problems in that domain.
- Knowledge base:** A knowledge base is a database that is constructed by the knowledge engineer and an expert to hold specific information and rules about a certain domain.
- Rule-based system:** A type of knowledge representation in which knowledge about a domain is expressed in rules that describe relationships between.

AN APPARATUS FOR RAPID MICROWAVE SAMPLE DECOMPOSITION

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A. Introduction

There is little doubt that the speed of analysis offered by many modern elemental analysis instrumentation systems is orders of magnitude faster than traditional (i.e., open-vessel, hot plate) sample digestion procedures. Therefore, digestion methodologies and instrumentation that offer high throughput are of paramount importance, especially for laboratories that must handle large numbers of samples.

The goal of this work is the development of rapid (i.e., less than 5 min) stopped-flow digestion instrumentation and methodology for botanical and biological samples of interest to the Ontario Ministry of the Environment (MOE). As in our earlier work [1, 2], a Teflon tube serves both as a sample container and as a digestion vessel. Besides the advantages mentioned above, the closed vessel, elevated temperature and pressure approach used here minimizes the risks of sample cross contamination when digesting multiple samples simultaneously and of acid fumes attacking the oven components. It also offers additional safety protection to personnel by limiting exposure to hazardous acid fumes and by minimizing reagent handling. Ease of automation is, perhaps, the most important advantage of this approach.

B. Instrumentation

A block diagram of the instrumentation developed in this work is shown in Fig. 1. The system consists of a peristaltic pump, two high pressure valves, a microwave oven, a "tube assembly", a pressure gauge and a temperature transducer.

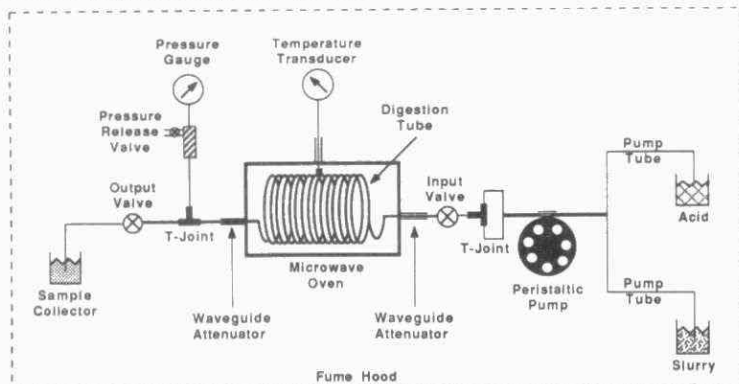


Fig. 1. Block diagram of the prototype tube-based microwave digestion system.

A slightly-modified (Fig. 2), domestic-type, commercially available microwave oven (model EXR-1690C, Toshiba Corp., 1-1, Shibaura 1 - Chome, Minato-Ku, Tokyo 105) is utilized. The power is adjustable in 9 steps, from 1 ("Low" corresponding to a power of about 70 Watts) to 9 ("High" or "Full" which is equivalent to a power of approximately 700 Watts). The heating time is programmable via front panel push-buttons and can be set from 1 sec to 99 min and 99 sec.

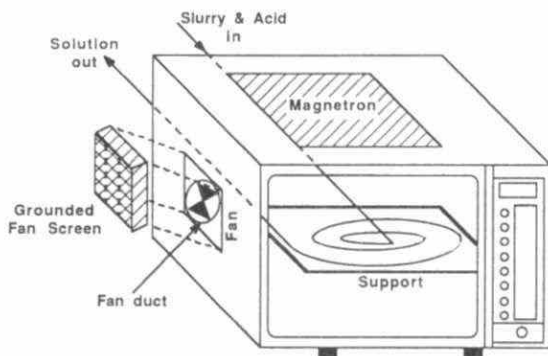


Fig. 2 Microwave oven set-up.

A Teflon PFA tube (perfluoroalkoxy, a chemically inert, nonporous tetrafluoroethylene with a fully fluorinated alkoxy side chain available from Cole-Palmer Instrument Co, Chicago, IL) with an ID of 1/4" and an OD of 5/32" serves as the digestion tube. According to manufacturer's specifications, it can withstand pressures of 421 psi and temperatures of 260° C. The tube, 13.8 ft (~420 cm) in length between the input- and output-valves, is coiled in 6 turns and is placed facing the magnetron, as shown in Fig. 2. This arrangement was chosen in order to take full advantage of the power delivered from the magnetron to the sample. A sample plug is pumped into the center of the coil. During digestion the sample slowly rotates inside the coiled tube due to pressure differences developed on either side of the sample plug. Fortuitously, this rotation serves as a stirring mechanism and also helps reduce the effects of non-uniform heating due to "hot spots".

After repeated use, for example, more than 100 times, the digestion tube showed visible signs of aging, such as yellowing, particularly at the T- and valve-joints and was replaced for safety reasons. In addition, a yellowish/brown coating and dark spots were visually observed inside the tube and in the interiors of the valves and the tube joints. These were attributed to undigested organic material. Some preliminary results indicate that the tube may have to be replaced more frequently due to accumulation of undigested material, which may give rise to memory effects, rather than due to aging or thermal/mechanical stress.

All measurements were performed using a Thermo Jarrel-Ash (Franklin, Massachusetts) model ICAP-61 inductively coupled argon plasma optical emission spectrometer. This computer controlled, 0.75-m, 34-channel polychromator system, is capable of determining 32 elements simultaneously.

C. Experimental

1. Reference Materials. The methodology was developed using "V85-1" and was tested using "Norway maple" and "White birch" botanical reference materials provided by the MOE (Rexdale facility). Although there are no certified values for these samples, the values reported here are the average quoted by the MOE. These were obtained using a 3 h long open-vessel digestion and analysis by ICP-AES [3]. Because the MOE and other environment monitoring laboratories are interested in trace elements that are environmentally available, their digestions are typically not brought to completion [4].

2. Procedure. Approximately 0.35 g of powdered sample is accurately weighed into a glass beaker and 20 mL of de-ionized water is added to it. The resultant slurry is continuously and rigorously stirred and then pumped, with both valves open (Fig. 1), into the digestion coil simultaneously with about 20 mL of acid or acid mixture. The valves are then closed and the sample is heated either at high power or using a power program (i.e., full power for 2 min followed by power level 5 for 3 min) for a pre-determined period of time. After digestion, the sample is allowed to air cool for several minutes. The exhaust valve is then opened to relieve pressure and the effluent is quantitatively transferred to the collection vessel.

Depending on power program and digestion time, the digests may contain unspecified amounts of undigested residue. Samples with residues are filtered, washed with distilled water, the filtrate is diluted to volume and analyzed by ICP-AES. All concentrations reported here are the average of five repeats and refer to dried samples. The moisture content was between 4% and 5%.

The digestion tube was thoroughly cleaned by a high speed flush with a water plug followed by a flush with an acid plug and a water plug. When changing sample types, the tube was cleaned by following the sample treatment procedure using only a water-acid mixture and by rinsing it with a water plug. The adequacy of this approach to eliminate memory effects is under investigation.

For the open-vessel work, approximately 0.35 g of sample were accurately weighed in an conical flask and mixed with 20 mL of distilled/de-ionized water and 20 mL of acid. The watch-glass covered flask was placed in a Pyrex vacuum desiccator (without the desiccant) which was subsequently placed in the microwave oven where it was heated for about 6 minutes. In order to vent acid fumes and to provide additional protection of the electronics and the magnetron, the vacuum port of the desiccator was connected to tygon tubing. The tube was routed, through one of the access ports cut on the back of the oven, to the fume hood. An open 100 mL beaker of water was placed in the oven in order to protect the magnetron from reflected power.

3. Safety. Safety was a key concern in operating this system. The following criteria were set: minimum radiation leakage (i.e., $<5 \text{ mW/cm}^2$ measured at 5 cm from the oven or any tube or cable emerging from it), no acid fumes in the microwave cavity and maximum operating pressure and temperature of 125 psi and 230°C . Although the tube assembly was safely tested and briefly operated at pressures as high as 200 psi, the choice of a lower operating pressure for routine operation was dictated by the weakest links in the tube assembly, namely the tube-to-valve and the tube to T-joint connections. According to the manufacture's specifications this is only 125 psi.

Due to the modifications of the oven (i.e., access ports) radiation leakage was an important consideration and was extensively monitored using a sensitive microwave power meter. Typical values ranged below 0.2 mW/cm^2 .

The final temperature of the sample in the digestion tube was measured in order to avoid placing excessive thermal stress on the tube. It was measured using a copper-constantan thermocouple encapsulated within a thin layer of glass and was held in place at about the middle of the digestion tube with a T-joint. The thermocouple leads were attached to a shielded and grounded cable. Regardless of power program and digestion time the temperature never exceeded the safety limit.

Due to the 125 psi pressure constraint, pressure was monitored in real-time. It was measured using a conventional pressure gauge and readings were manually taken at one minute intervals. The results for various acids, a 0.35 g of V85-1 botanical sample and high power are shown in Fig. 3. The steep increase observed when a mixture of HNO_3 and H_2O_2 are utilized indicates rapid formation of gaseous products and, although it may have to be correlated with temperature and H_2O_2 gaseous decomposition products, it also indicates a faster attack of botanical samples.

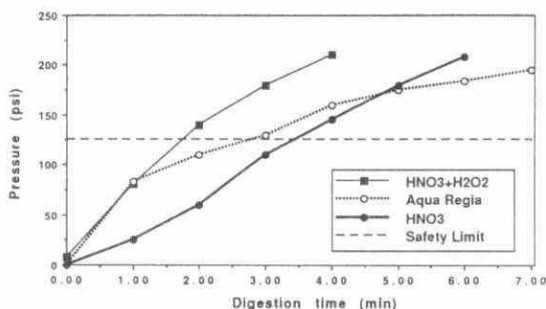


Fig. 3 Digestion tube pressure as a function of heating time for various acid mixtures.

From the results shown in Fig. 3 it can also be concluded that regardless of acid mixture, the 125 psi safety limit is reached in less than 3 min. And because aqua regia resulted in more complete digestions in the shortest time, it was the acid of choice and was used throughout.

However, when short digestion times are used (i.e., < 2 min) relatively large amounts of undigested material was visually observed to remain in the digestion tube and to settle in the collection vessel. Therefore, longer digestion times may have to be used in order to obtain a complete digestion (i.e., one that results in clear and colorless solutions with no visible signs of residue).

D. Results and Discussion

1. Power program and digestion time. A power program was utilized in order to increase the digestion time and to obtain a more complete digestion without exceeding the pressure limit. More specifically, V85-1 samples were digested by applying full power for 2 min followed by a lower power level for another 3 min. Pressure was monitored in real-time as before. The results are shown in Fig. 4. From these it can be concluded that there exists an almost linear relationship between applied power and pressure and that lower power levels result in longer digestion times, as expected. However, even when a power level 5 is used, resulting in an additional 3 min of digestion time, the amount of undigested organic material is still considerable.

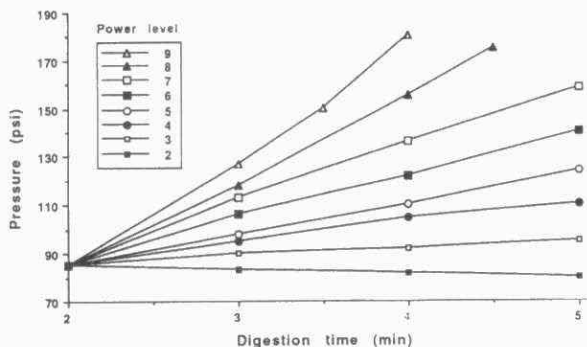


Fig. 4 Digestion tube pressure for various power levels (see text for discussion).

2. Power program and digestion time for complete digestion. The conditions for complete digestions were established by applying a series of power programs to V85-1 botanical slurries and aqua regia and by monitoring pressure in real-time. The experiment ended when all organic material was digested and a clear and almost colorless solution was obtained. The results are shown in Fig. 5. For power program 1 (Fig. 5, circles), high power is applied for 2 min, power is then turned off until pressure drops below 100 psi and high power is again applied until pressure exceeds 150 psi and so on until a complete digestion is obtained. For power program 2 (Fig. 5, squares), high power is applied for 2 min followed by the application of power level 4 for 7 min followed by power level 5 until the end of the digestion. Similarly, power program 3 (Fig. 5, triangles) is obtained by applying high power for 2 min followed by continuous application of power level 5 until the end of the digestion. From these results it can be concluded that program 3 results in a complete digestion in about half the time required by program 1, thus providing considerable time-savings. However, in terms of applied microwave energy, the power programs described above are essentially equivalent. This can be easily explained by considering programs 1 and 3. Excluding the initial 2 min period, full power is applied for a total of 10 min (program 1) whereas a power level 5 is applied for 20 min (program 3).

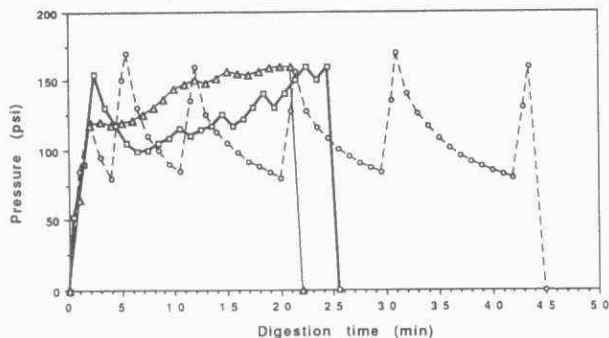


Fig. 5 Pressure versus digestion time for various power programs (see text for discussion).

However, a power level 5 is equivalent to a duty cycle of 50%, that is, full power applied half of the time. Thus, full power for 10 min is equivalent to power level 5 for 20 min. But, are complete digestions necessary in order to obtain 100% recovery of trace elements in botanical samples?

3. Elemental recoveries and digestion time. MOE V85-1 botanical samples were digested with aqua regia for 2-, 4-, 8-, 16- and 32-min. The digested samples were analyzed for Al, B, Ba, Cd, Cu, Fe, Mg, Mn and Zn. The results are summarized in Fig. 6. From these it can be concluded that trace metals are fully recovered in two minutes at full power when V85-1 samples are used. However, to further substantiate this conclusion, the question of individual elemental recoveries must be first addressed.

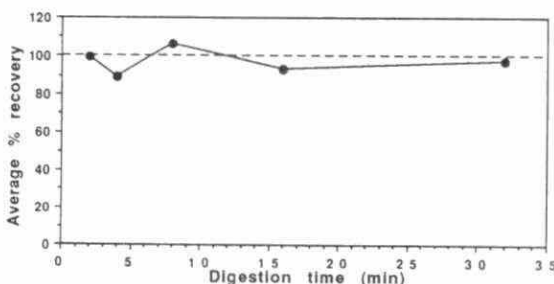


Fig. 6 Average recovery versus digestion time for V85-1 samples (see text for discussion).

In order to test for the individual elemental recoveries, V85-1 samples were digested for 2 min at full power. The results are shown in Table 1. With the exception of Al which is under-recovered and of Ba which is over-recovered (both with respect to the MOE values), the average concentrations and the standard deviations are in agreement with the MOE values. No explanation can be offered at this point in time for the Al and Ba concentrations. In order to obtain "total" digestions and to establish a "reference" value, V85-1 samples are now being digested in the coiled tube for 32 min using a power program.

Table 1. Analysis of V85-1 reference botanicals.

Element	Coiled Tube (T) ($\mu\text{g/g}$)	Open (O) Vessel ($\mu\text{g/g}$)	MOE Value ($\mu\text{g/g}$)	% Recovery		
				(T/O)	(O/MOE)	(T/MOE)
Al	54 \pm 5	56 \pm 3.9	100 \pm 11	96	56	54
Ba	13 \pm 0.4	14 \pm 0.3	10 \pm 0.7	93	140	130
Ca	12000 \pm 550	13000 \pm 470	12000 \pm 580	92	108	100
Cu	14 \pm 1	16 \pm 0.8	13 \pm 0.8	88	123	108
Fe	255 \pm 13	280 \pm 8.5	230 \pm 18	91	122	111
Mg	2300 \pm 88	2500 \pm 75	2100 \pm 130	92	119	110
Mn	67 \pm 2.5	68 \pm 2.0	60 \pm 4.6	99	113	117
Zn	140 \pm 6.4	160 \pm 0.4	140 \pm 11	88	114	100

In order to further substantiate the results obtained when short digestion times are used and to provide a basis for comparison [5], V85-1 samples were digested in the microwave oven using

open-vessels (Table 1). From these results it can be concluded that the tube system recovers in 2 min about as much as open-vessels in 6 min, thus demonstrating the validity of our approach.

A comparison of short-time digestions with the MOE values reveals that, except for Al, the tube digestion system recovers in 2 min more than hot-plate digestions do in hours. From the low standard deviations reported in Table 1 it can be concluded that highly reproducible digestions are obtained with this system. Therefore, for a difficult-to-digest element, such as Al, a correction factor may be applied with a reasonable degree confidence. In summary, from the results presented thus far it can be concluded that for V85-1, a 2 min digestion provides elemental recoveries of about 100% for most elements.

4. Testing the methodology. The methodology developed thus far (i.e., aqua regia, 2 min digestion, full power) was tested using MOE Norway maple and White birch botanical reference materials. In order to verify the results obtained using the tube system and short digestion times, these samples were also digested in open-vessels. The results are shown in Table 2 for White birch and in Table 3 for Norway maple. In general, the results reported here are in good agreement with those reported by the MOE. In summary, and much like other microwave digestion systems [5, 6] elemental recoveries appear to be sample type dependent. However, more work remains to be done in order to further substantiate this conclusion.

Table 2. Analysis of Norway maple botanical samples.

Element	Coiled Tube (T) ($\mu\text{g/g}$)	Open (O) Vessel ($\mu\text{g/g}$)	MOE Value ($\mu\text{g/g}$)	% Recovery (T/O) (O/MOE) (T/MOE)		
Al	130 \pm 19	100 \pm 5.8	180	130	56	72
Ba	18 \pm 0.76	18 \pm 0.59	14	100	129	129
Ca	28000 \pm 1700	28000 \pm 1100	28000	100	100	100
Cu	9.8 \pm 0.31	9.6 \pm 0.44	8	102	120	122
Fe	420 \pm 16	460 \pm 13	420	91	110	100
Mg	2500 \pm 140	2600 \pm 82	2200	96	118	114
Mn	56 \pm 0.1	53 \pm 18	47	106	113	119
Pb	120 \pm 4.1	130 \pm 3.4	95	92	137	126
Zn	42 \pm 1.9	44 \pm 1.6	40	95	110	105

Table 3. Analysis of White birch botanical samples.

Element	Coiled Tube (T) ($\mu\text{g/g}$)	Open (O) Vessel ($\mu\text{g/g}$)	MOE Value ($\mu\text{g/g}$)	% Recovery (T/O) (O/MOE) (T/MOE)		
Al	24 \pm 2.6	24 \pm 2	42	100	57	57
Ba	84 \pm 0.95	100 \pm 3.4	86	84	116	98
Ca	14000 \pm 450	16000 \pm 370	14000	88	114	100
Cd	0.8 \pm 0.11	0.99 \pm 0.07	0.9	81	110	89
Cu	5.6 \pm 0.77	5.7 \pm 1.2	5	98	114	112
Fe	61 \pm 2.5	68 \pm 2.4	59	90	115	103
Mg	2100 \pm 75	2500 \pm 67	2100	84	119	84
Mn	611 \pm 16	704 \pm 19	600	87	117	87
Zn	180 \pm 8.5	220 \pm 7.3	200	82	110	90

E. Conclusions

In this preliminary study, a stopped-flow microwave digestion prototype system has been developed. Precise and quantitative digestions of trace elements in botanical samples are obtained in 2 min using straight forward methodology and inexpensive instrumentation. The methodology is being tested with NBS botanical and biological standard reference materials (SRMs). Initial results indicate that these SRMs can be easily digested in 2 min providing 100% recoveries for most elements. In order to test for a possible general applicability of stopped-flow digestions, this study is being further expanded to cover other sample types as well, for example, geological MOE and NBS SRMs. Some preliminary results show that even with short digestion times, the system can digest MOE soil samples and NBS coal fly ash. In this case, however, the acid mixture must also contain 1 to 2 mL of HF.

The current shortcomings of the system stem from the use of relatively large volumes of acids, from tube contamination with consequent memory effects and from delays arising during cooling the digests. These are under study and appear to be easy to solve. The additional safety precautions required for routine operation, for example, installation of waveguide attenuators in all access ports and a pressure release valve (Fig. 1) are also being addressed.

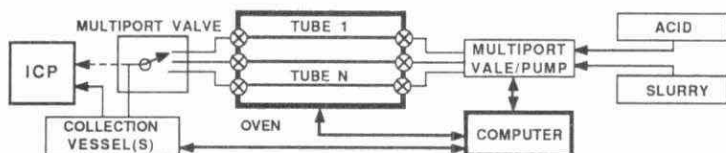


Fig. 7 Diagram of the proposed 'next generation' stopped-flow digestion system.

The findings reported here and the experience gained in operating this system will be used as the basis for the development of a computer controlled system operating asynchronously on multiple tubes/samples (Fig. 7). This system will be subsequently tested with some difficult-to-digest samples, such as soils and geologicals. Further into the future, automation of sample handling, preparation of slurries and even a direct interface to the ICP are envisaged (Fig. 7). Development of such a system is anticipated to give rise to an intelligent sample processor for the ICP [7].

References

1. E.D. Salin and F.H. Li, Paper D6, Proceedings of the Ontario Ministry of the Environment, Technology Transfer Conference, Toronto, Ontario, Nov. 20-21, 1989
2. E.D. Salin and B. Liu, Paper DP3, Proceedings of the Ontario Ministry of the Environment, Technology Transfer Conference, Toronto, Ontario, Nov. 28-29, 1988
3. D. Boomer, Personal communication, Montreal, July 1990
4. C.G. Millward and P.D. Kluckner, *J. Anal. Atom. Spectrom.*, 4, 709 (1989)
5. H.M. Kingston and L.B. Jassie, Eds., *"Introduction to microwave sample preparation"*, ACS Professional Reference Book, ACS, Washington, DC (1988)
6. H. Matusiewicz and R. Sturgeon, *Prog. Anal. Atom. Spectrosc.*, 12, 21 (1989)
7. V. Karanassios, Ph.D. Thesis, University of Alberta, 1988

AN ELECTROTHERMAL VAPORIZATION SYSTEM FOR THE DIRECT ANALYSIS OF SOLIDS BY ICP-AES

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BACKGROUND

In our laboratory we have studied sample introduction systems for atomic spectrometry for over a decade. The original work centered on the use of DSI (Direct Sample Insertion) techniques. These techniques involve inserting a sample carrying probe into the plasma along the axial channel. Our original work was with liquid samples using wire loops [1] and electrochemical preconcentration techniques [2]. This work provided the background for a move into direct solid sample analysis by DSI for both atomic emission [3] and mass spectrometry [4].

Considerable solids oriented work on the DSI using both cups and wire restrained pellets has demonstrated that the technique has very low detection limits, yet requires the use of standard additions in cases where the matrix is complex [5-7]. At the onset of the project, we targeted geological materials. These often have a silicon matrix and so require considerable sample preparation, often with HF, and consequently were considered appropriate candidates. If the material is inserted into the plasma in a graphite/sample pellet with a high proportion of the analyte, a Si cloud will carry a great deal of the analyte through the plasma without excitation. The large Si vapor cloud appears to alter normal flow patterns in the plasma and changes the excitation conditions. However, volatile toxic elements (i.e., Cd, Hg and Pb) emerge before the Si cloud and are measurable. Dilution of the sample in more graphite results in much better accuracy but drastically reduces detection limits since less sample is introduced into the plasma.

In an attempt to modify the chemistry of the system, we have used various additives including AgCl, NaF and CuCl to produce volatile halides. The NaF causes a rather spectacular breakdown of the Si in a short time but again causes significant disruption of the plasma while carrying a great deal of the analyte with it.

To summarize, we felt that a number of general lessons were learned that could be applied in the development of a new type of solid sample introduction system.

1. Large amounts of analyte should be vaporized. This improves detection limits in proportion to the mass of the analyte (disregarding the interference effects mentioned above).
2. The vapor must be forced through the center of the plasma.
3. The vapor should be generated in such a way that it causes a minimal disruption of the plasma.
4. Chemistry can be used to modify the sample breakdown processes, but must not be allowed to distress the plasma.

In the following section we will discuss the results obtained with a system designed with the above lessons in mind.

RATIONALE

Given the requirements for large mass and minimal disruption of the plasma, we developed a system which uses the "Separate Sampling and Excitation" principle implemented so well in the Thermo Jarrell Ash® Spark (sampling)/ICP (excitation) system. Unfortunately, the spark in these systems only vaporizes a relatively small portion of the sample, resulting in relatively high (poor) detection limits. Our approach involves electrothermal heating of a graphite/sample pellet. The ETV (electrothermal vaporization) configuration, Figure 1, allows the sample to be "processed" remotely from the plasma. Analyte vapor is then transported to the plasma where the use of a traditional torch/injector configuration forces the vapor cloud through the center of the plasma. The use of a pellet, rather than the conventional sample cup or tube, allows large amounts of sample to be heated very rapidly due to the intimate contact between the resistively heated graphite and the sample.

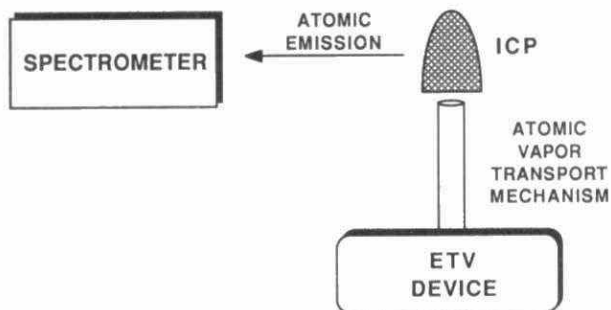


Fig. 1 Illustration of "Separate Sampling and Excitation".

EXPERIMENTAL

The ETV apparatus is illustrated schematically in Figure 2. The present configuration is a first prototype and was developed with the primary goal of expediency. A conventional Perkin Elmer HGA 2200 furnace assembly was used nondestructively by adding the components illustrated in Figure 2. Our goal was simply to test the principle, and no particular attention was paid to the gas flow patterns. We did place the pellet in between the entrance and exit gas ports, however, we expected that there would be considerable "dead volume" in an unswept design such as this.

Pellets were hand pressed into a 4 mm diameter cylinder 9 mm long using a Parr press and Spex spectroscopic grade dc arc graphite in a ratio of 9 graphite to 1 sample. The pellets are ramped through a short drying cycle to remove moisture and then raised rapidly to 1250°C to produce a short duration analyte pulse in the plasma. A temperature of 100°C was used for standards (oxides) while 300°C was used to ash botanical samples. MOE V85-1, Norway Maple and White Birch samples were used to evaluate the samples with real samples.

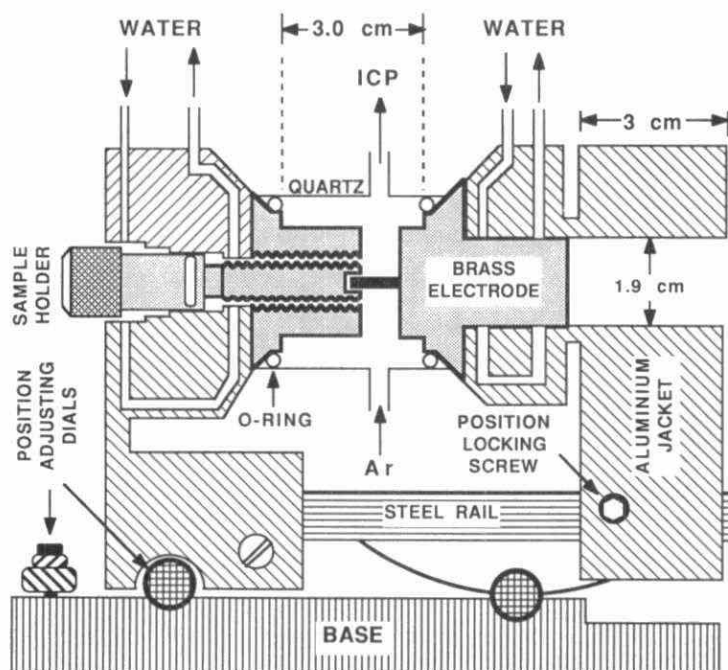


Fig. 2 Illustration of ETV device.

Measurements were made on an older Jarrell Ash simultaneous multichannel spectrometer modified by Technical Services Laboratory of Toronto. The modifications included the addition of a galvanically driven refractor plate with direct computer control over the drive and data acquisition. Both the DSI and ETV experiments produce analyte clouds in a very narrow time window. The modified spectrometer system allows very rapid on and off line measurements which are often essential to this type of work. The software/hardware in this configuration provides a degree of flexibility which is not possible in commercial systems with which we are familiar.

PERFORMANCE

Exemplary detection limit data for several elements in single element mixtures are presented in Table I. Precision data is presented in Table II for standards. Both are obviously very encouraging. We find it very gratifying to have solid detection limits which are comparable to those obtainable with liquid techniques. Note that the Jarrell Ash plasma detection limits are for liquid samples. To digest a sample, a factor of roughly 10 in dilution would be expected subsequently raising the detection limit in the solid by a factor of 10.

Table I. Detection limits.

Element	<u>Pellet-ETV system</u>		<u>Jarrell Ash ICAP 61</u>	
	Line (nm)	DL (ppb)	Line (nm)	DL (ppb)
Pb	220.3	4.4	220.3	26.5
Zn	425.4	17.0	213.8	0.4
Cd	228.8	5.0	228.8	0.7

Table II. Reproducibility.

Element	Peak Height (%RSD)	Peak Area (%RSD)
Pb	4.0	4.9
Zn	3.0	*
Mn	9.5	13.7
Cd	5.5	8.2

* No data available due to multiple peaks

Typical time profiles are presented in Figure 3. It is interesting to note that many of the elements evolve at quite different times. This is similar to what we have observed with our DSI system. We generally consider this beneficial, since it allows the spectral interference from one element to pass through a different time window. It is important to note, however, that real sample matrices may drastically alter the time performance and nullify this apparent advantage. These experiments were run with a final temperature of 1250°C, higher temperatures may force the analytes out more quickly. This could be advantageous in overcoming matrix effects, but may also result in an unwanted pressure pulse. The system may also allow us to use matrix modifiers such as NaF without the disruption to the plasma which we experienced when using DSI probes in the plasma.

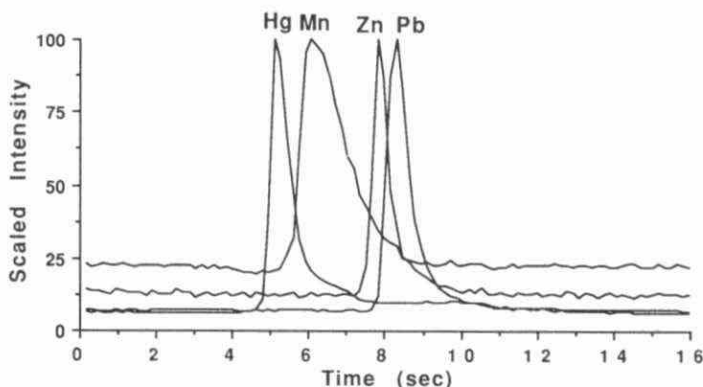


Fig. 3 Typical analyte emission temporal behavior and "volatility" sequence.

Table III. Analysis of MOE botanical reference materials for Pb and Zn.

Sample Type	Element: Pb		Element: Zn	
	Found Conc.	MOE Value	Found Conc.	MOE Value
V85-1	17 ppm	19 ppm	46 ppm	14 ppm
White birch	350 ppb	400 ppb	58 ppm	20 ppm
Norway maple	42 ppm	40 ppm	48 ppm	40 ppm

We tested the system on several MOE sample types for two elements, Zn and Pb (Table III). These first results are quite encouraging, although our experience [5, 6] would lead us to expect that botanical samples should be relatively easy sample types. Our next step will be to explore more difficult sample types such as the geological MESS and BCS or NBS Coal Fly Ash. These will provide an interesting test of the Separate Sampling and Excitation principle as applied to ETV vaporization.

REFERENCES

1. R. L. A. Sing, E. D. Salin (1989), "Introduction of liquid samples into the inductively coupled plasma by direct insertion on a wire loop", *Anal. Chem.*, **61**(2), 163-9.
2. M.M. Habib, E.D. Salin, "A Flow-through Electrolytic Cell for Direct Insertion into an Inductively Coupled Plasma", *Spectrochim. Acta* (accepted)
3. R.L.A. Sing. Ph. D. Thesis, "Direct Insertion of Liquid and Solid Samples into the ICP", McGill University (1986)
4. L. Blain, E.D. Salin, D.W. Boomer (1990), "A Novel Probe Design for the Direct Insertion of Solid Samples in the Inductively Coupled Plasma for Analysis by Atomic Emission and Mass Spectrometry", *J. Anal. At. Spectrom.*, **4**(8), 721-5.
5. L. Blain. Ph. D. Thesis, "Solid Sample Analysis with the Direct Sample Insertion Device", (in preparation)
6. L. Blain, E.D. Salin, "Analysis of Geological Materials by ICP-AES with a Direct Sample Insertion Device", (in preparation)
7. E.D. Salin (1990), Ontario Ministry of the Environment, Final Report for project 270 RR.

FLOW INJECTION PRECONCENTRATION/DIRECT SAMPLE INSERTION FOR TRACE ANALYSIS BY ICP-AES AND ICP-MS

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INTRODUCTION

As our knowledge of the environment increases, our need for better analyses grows. The inductively coupled plasma using either optical or mass detection, would appear to an option worth exploring. However, to be of maximum value, the detection limits of the ICP-AES need to be improved and the ICP-MS suffers from serious matrix effects. We have undertaken the development of a system which combines two technologies, flow injection analysis (FIA) and direct sample insertion (DSI) to obtain sample clean up and detection limit improvements. If successful, this system will extend working ranges and minimize matrix effects for both types of instrumentation.

The union of flow injection analysis (FIA) with inductively coupled plasma atomic emission spectrometry (ICP-AES) has been reported in the literature ¹⁻⁶. Standard pneumatic nebulization using cross-flow or concentric nebulizers are usually directly coupled to the output of the FIA system. This has given good results but the small discreet plug from the FIA is diluted in the spray chamber. It is the low transport efficiency (reported to be between 1-5%²) of these nebulizers that has lead Gustavsson to remark; "Consequently an interface between an FIA device and the ICP, capable of utilizing the full potential of the combination, has yet to be developed."³

LaFreniere and co-workers have developed a direct injection nebulizer (DIN) that achieves 100% sample introduction efficiency and is compatible with typical FIA flow rates. They report some detection limit improvements but it seems to suffer from solvent loading problems.^{4,5}

Thermospray interfacing, which has been used to combine liquid chromatography with mass spectrometry, has also been applied to FIA/ICP-AES. With thermospray the liquid effluent is forced through an electrically heated stainless steel capillary producing a super heated aerosol carried in a jet of vapour. Some detection limit improvements were reported but the system is still undergoing design changes.⁶

Electrothermal vaporization (ETV) has not yet been reported in combination with FIA. It has however been well established as a sample introduction method for small volume liquid samples to ICP-AES using both graphite tubes,⁷ wire loop atomizers⁸ and metal filaments⁹. In ETV, control of the drying step is possible.

In our original proposal we presented direct sample insertion as a viable way to introduce pre-concentrated samples from our FIA system to the plasma. Newly designed graphite cups of overall reduced mass have been described as being able to achieve an order of magnitude improvement in detection limits.¹⁰ As reported by Sing and Salin, wire loops give detection limit improvements of 1-2 orders of magnitude based on one drop.¹¹ Since we hope to be able to collect the total volume (approx. 100 -250 μ L) from the FIA and dry it onto the loop (or into the cup), essentially another pre-concentration, our detection limits compared to nebulization of this small volume should be improved to an even greater extent.

Table 1 compares the three ways of introducing liquid samples to the ICP.

Table 1 Discrete Liquid Sample Introduction Techniques for ICP-AES

Method	Advantages	Disadvantages
Wire loops	Superior detection limits Already interfaced with the ICP-MS at the MOE	Spectral interferences (W loop) Difficult interface -possible loss of sample -long drying times
Graphitic cups	No carbide formation Time resolution of elements Easy interface - batch mode drying	Carbide formation with refractory elements
ETV	Specially machined cups x 10 better detection limits Maximal control of drying conditions Easy interface Good detection limits	Overall detection limits higher than wire loops Carbide formation Some memory effects observed

EXPERIMENTAL

Flow Injection Analysis System Developed

The FIA system shown in Figure 1 is based on the chemistry of preconcentration of Chelex-100 ion exchange resin with a strong acid as the eluant. A recent critical examination of Chelex-100 for the enrichment of sea water found it to be a good choice if enough attention is given to several critical parameters.¹² This has also been our experience and the applicability of Chelex-100 to a wide range of target metals, as well as its ability to reduce matrix effects by selectively rejecting cations such as Na, Ca and Mg, make it a good candidate for several sample types.

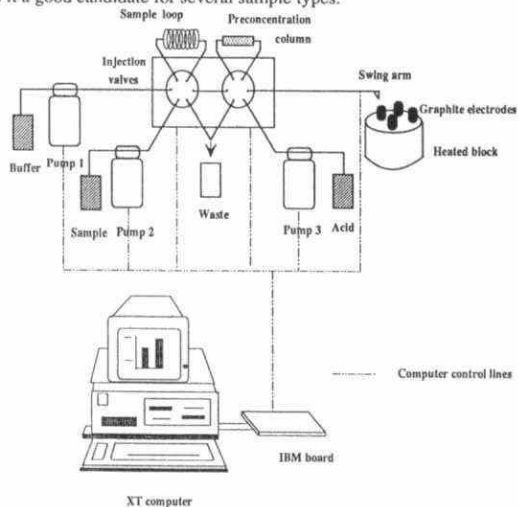


Figure 1. Flow Injection System Developed

There has recently appeared on the market a preconcentration unit, to be used as a front end to an ICP-AES spectrometer, marketed by Dionex Corporation. The column used in this system contains a resin with the same macroporous polystyrene-divinylbenzene iminodiacetate backbone as Chelex-100 but with a higher degree of crosslinking. It is this higher degree of crosslinking that solves some of the difficulties such as the 100% swelling that Chelex-100 undergoes with a change in pH.¹³ For this reason columns based on this resin will also be evaluated. The similarity between the resins means that the optimal experimental parameters are comparable.

DSID Sample introduction

Graphite cups

Standard graphite cups such as those used by Shao and Horlick¹⁴ were first tried with the stepper motor direct sample insertion device as described by Sing and Salin¹¹. The spectrometer used was a Thermo Jarrell Ash multi channel with software and hardware modifications made by Technical Services Laboratory¹⁵. The operating conditions are listed in Table 2. The detection limits, as discussed in former reports, obtained without optimization were comparable or an order of magnitude worse than those obtained by nebulization with the same system.

Umemoto and Kubota recently reported on the results of using specially machined graphite cups with relatively thin walls (0.5 mm) and approximately 1 mm diameter supporting rods. They found an order of magnitude increase in detection limits over pneumatic nebulization.¹⁰

The dimensions of the thin walled graphite cup as compared to that used previously are given in Table 2. Preliminary experiments with graphite cups that had only a 1 mm stem thickness indicated that they would be too fragile for routine work. The graphite rod thickness used was 2 mm which gave slightly lower signal levels, on the order of 5%, and were considerably more robust.

Table 2 ICP Operating conditions (Graphite cup)

Spectrometer	Thermo Jarrell Ash (modified by TSL laboratories)		
ICP parameters		DSI parameters	
Forward power	1.25 kW	Drying height	25 mm below TOLC
Reflected power	< 50 W	Drying time	30 sec
Plasma gas flow rate	14 L min ⁻¹	Insertion depth	2 mm above TOLC
Aux. gas flow rate	0.8 L min ⁻¹	Insertion time	45 sec
		Observation hgt	15 mm above TOLC
Cup Dimensions:			
	Conventional	Thin walled	
Cup depth(mm)	4.8	6.0	
Rod thickness(mm)	3.2	2.0	
Wall thickness(mm)	0.8	0.5	
Cup diameter (mm)			
i.d.	4.57	5.18	
o.d.	6.0	6.0	

* TOLC = top of the load coil

Wire Loops

The wire loops used were formed from rhenium wire, instead of the tungsten used by Sing and Salin in previous work¹¹, as a means to reduce potential spectral interferences.

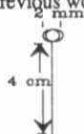


Figure 2 Re wire loop

The wire was 0.5 mm in diameter and was formed into two side-by-side 2 mm diameter loops on the end of a 4-cm stem, this is similar in dimensions to the traditional W loop (see Figure 2). Ten μL samples were applied with a Eppendorf pipet. The rest of the operating conditions are listed in Table 3.

Table 3 ICP Operating Conditions (Wire loop support)

Spectrometer		Thermo Jarrell Ash (modified by TSL laboratories)	
ICP parameters		DSI parameters	
Forward power	1.5 kW	Drying height	22 mm above TOLC
Reflected power	< 50 W	Drying time	20 sec
Plasma gas flow rate	14 L min ⁻¹	Insertion depth	2 mm above TOLC
Aux. gas flow rate	0.8 L min ⁻¹	Insertion time	5 sec
		Observation hgt	15 mm above TOLC

RESULTS AND DISCUSSION

Flow Injection System

The full details of the preconcentration chemistries attempted have been previously reported¹⁶. To recap; the ion exchange resin, Chelex-100 was evaluated with both acid elution and the use of other complexing agents as eluting agents. Nitric acid elution gave pre-concentration factors of 33 for Cu, 22 for Cd and 24 for Zn. When EDTA was used as the eluant, respective enrichment factors of 24 and 22 were obtained for Cd and Pb. The best pre-concentration factor, a value of 50, was obtained when L-cysteine was used to elute Cu from the column. The only caveat in this case is that a reduction step makes this application element specific.

Direct Sample Insertion

Thin-walled Graphite Cup

The results obtained with the thin-walled graphite cup indicate that there are detection limit improvements both over regular nebulization and standard graphite cups. The detection limits are reported in Table 4.

Table 4 Detection limits with Thin-walled Graphite Cup (ppb)

Element/	Line (nm)	Pneumatic Nebulization	Graphite Cup (thin walled)
Cu	324.7	8.4	0.86
Cd	228.8	9.3	2.1
Pb	220.3	28	0.85
Zn	425.4	82	0.62

* peak area, 50 μ L samples
3 sigma detection limits

Wire loop

The first results obtained with the rhenium wire loop indicate that it is a good alternative to tungsten. There was no interference observed for a blank of distilled deionized water at the wavelengths of any of the elements analyzed (Cd, Cr, Cu, Mn, Pb, V, Zn).

The preliminary detection limits are shown in Table 5. It should be noted that the results on the rhenium loop were not obtained under optimized conditions. A factor of improvement between 3 and 4 was obtained for most elements. There is every reason to expect that, with optimization, a factor of 10 (i.e. that found by Sing and Salin) improvement in detection limits will be realized.

The rhenium loop was inserted into the plasma more than 60 times over the time period of these initial experiments with apparently no deterioration of the loop. In this way, it proves to be a better material than tantalum.

Table 5 Detection limits with Wire Loop (ppb) * peak area, 10 μ L samples

Element/	Line (nm)	Pneumatic Nebulization	Wire loop (rhenium)
Cr	267.7	28	9.2
Mn	293.9	7	2.2
Pb	220.3	28	7.3

FIA Combined with DSI

The flow injection system, as shown in Figure 1, was used to preconcentrate 5.0 mL of standard aqueous solutions into an acid matrix which was collected and then dried into a thin-walled graphite cup using an infrared lamp. The preconcentration columns used contained either Chelex-100 (100-200 mesh) or the MetPac CC-1 resin (50-100 μ m) as developed by Dionex. The length of the column was 2.0 cm with a 2.30 mm inner diameter constructed from Tygon tubing. The buffer used was 0.5 M

ammonium acetate (pH = 5.5) at a flow rate of 2.0 mL; the acid is nitric (2.0 M) at a flow rate of 1.2 mL min⁻¹

The control program was written in Turbo Pascal 5.0 and allows for a flexible interface that uses an IBM 16 port I/O board to control up to 16 pumps or valves. Each step in the preconcentration process involves having the valves in a certain position and the pumps operating or not. Our input data files specify both the status of the pumps and valves and the length of time for the system to remain at that status. After the time has passed, as determined by external computer timing, the status of the pumps and valves is altered. The program used to preconcentrate the 5.0 mL sample volume is laid out in Table 6.

Table 6 Preconcentration program

time (sec)	V1	V2	P1	P2	P3	Action
150	1	0	0	1	1	1. Loading the sample loop and rinsing the column with acid
120	1	1	1	0	0	2. Conditioning the column with buffer
150	0	1	1	0	0	3. Loading the sample onto the column.
110	1	0	0	0	1	4. Eluting the column with acid and collecting the preconcentrated sample.

1 = ON / LOAD
0 = OFF / INJECT

Initial results with the combined system are positive. However, there seems to be considerable tailing of the elution peak which results in the analyte being over a greater volume. Future efforts will be concentrated on reducing the acid eluant volume by altering the column dimensions, shortening the connecting tubing and increasing the acid strength and/or flow rate.

CONCLUSIONS

The chemistry of preconcentration by flow injection analysis has been aptly demonstrated to work. The preconcentration factors vary with the amount of sample and time available and, of course, the experimental parameters.

Future work will concentrate on gathering the detection limit improvement data using standard samples. The FIA-DSI approach will also be applied to several real sample matrices to demonstrate some of its potential applications.

Direct sample insertion is a viable means of ensuring that one hundred percent of the mass of the desirable elements in the target sample are delivered to the plasma; freed by FIA from the interferents that may have originally been present.

REFERENCES

1. Greenfield, S. *Spectrochim. Acta*, Part B 1983, 38B, 93.
2. Greenfield, S. In *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, Eds Montaser, A.; Golightly, D.W., VCH Publishers, 1987, 155.
3. Gustavsson, A.G.T., Liquid sample introduction into plasmas, In *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, eds Montaser, A.; Golightly, D.W., VCH Publishers, 1987, 409.
4. LaFreniere, K.E.; Rice, G.W.; Fassel, V.A. *Spectrochim. Acta*, Part B 1985, 40B, 1495-1504.
5. Lawrence, K.E.; Rice, G.W.; Fassel, V.A. *Anal. Chem.* 1984, 56, 292-293.
6. Koropchak, J.A.; Winn, D.H. *Anal. Chem.* 1986, 58, 2561-2563.
7. Swaidan, H.M.; Christian, G.D. *Anal. Chem.* 1984, 56, 120-122.
8. Newton, P.; Davis, D.G. *Anal. Chem.* 1975, 47, 2003-2009.
9. Matusiewicz, H.; J. *Anal. At. Spectrom.*, 1986, 1, 171.
10. Umemoto, M.; Kubota, M. *Spectrochim. Acta*, Part B, 1989, 44B, 7, 713-723.
11. Sing, R.L.A.; Salin, E.D. *Anal. Chem.* 1989, 61, 163-169.
12. Van Berkel, W.; Overbosch, A.W.; Feenstra, G.; Maessen, F.J. *JAAS*, 1988, 3, 249-257.
13. Siriraks, A.; Kingston, H.M.; Riviello, J.M., *Anal. Chem.* 1990, 62, 1185-1193.
14. Shao, Y.; Horlick, G. *Appl. Spectrosc.* 1986, 40, 386-393.
15. Legere, G.; Burgener, P. *ICP Inf. Newsl.* 1987, 13, 521.
16. Moss, P.; Salin, E.D. *Conference Proceedings Technology Transfer Conference 1989, Analytical Methods Division, Paper D4* 1989.

Prereduction of Arsenic(V) to Arsenic(III), Enhancement of the Signal, and Reduction of Interferences by L-Cysteine in the Determination of Arsenic by Hydride Generation

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Since Holak¹ published his paper on the determination of arsenic by hydride generation-atomic absorption spectrometry, many papers have been published which deal with arsenic determination by arsine generation combined with AAS²⁻⁶, ICP-AES,^{3,4,7} and DCP-AES⁸⁻¹⁰. Since trivalent and pentavalent arsenic show different behaviour in the arsine generation process, several workers¹¹⁻¹⁴ have developed methods for selective determination of As(III) in the presence of As(V). On the other hand, because of the difference in sensitivity between the As(III) and As(V) in the hydride generation process,^{15,16} many workers have preferred to reduce As(V) to As(III) with various prereducing agents before arsine generation. The most popular prereductant is potassium iodide. It has been used in combination with ascorbic acid, which can prevent the oxidation of I^- to I_3^- by air or some other oxidant such as Fe(III)¹⁷. However, KI can only be used in strong acid media. The acid concentration is critical, for example, at concentrations of less than 0.3M, it failed to reduce As(V) to As(III) completely.^{13,17} Furthermore, some workers reported that, when using KI as prereductant, it took as long as 4-5 hours to reduce As(V) to As(III) completely at room temperature.^{17,18} Potassium iodide has also been used in combination with sodium sulphite,¹⁹ and with thiourea.²⁰ Thiourea alone has been used in dilute acid¹³ but caused competing reactions in the later hydride generation step. Takahashi *et al.*²² reported that, when mercaptoacetic acid was used as a prereducing agent, the

sensitivity in the determination of inorganic arsenic by atomic absorption spectrometry was lower than when potassium iodide was used.

For applications other than hydride generation, other prereducing agents have been used. Sodium thiosulphate alone²³ and in combination with sodium hydrogen sulphite,²⁴ and titanium(III) chloride²⁵ have been used to reduce arsenic(V) to arsenic(III) in solvent extraction methods that have been used in speciation studies. Sodium sulphite has been used in stripping voltammetry.²⁶

In our previous work,^{10, 27} we found that, when hydride generation was allowed to proceed for 20-30 seconds in 5 M HCl before arsine was stripped, peak heights may be used to determine the total (As(III) and As(V)) arsenic concentration. A delay column was necessary, for determination by DCP, to control the surge of hydrogen which would otherwise destabilize the plasma.

Although the hydride generation technique is relatively simple and has high sensitivity, it suffers from interferences that arise from certain metal ions in the sample solution.^{15, 28-32} We have found that L-cystine and L-cysteine are excellent reagents to reduce interferences in the hydride generation process for the determination of arsenic,²⁷ tin,³³ and germanium.^{34, 35} In addition, we have shown that L-cysteine can speed up the rate of reduction by sodium tetrahydroborate (III), thereby increasing the sensitivity in the determination of Ge.³⁴

In this paper, we report our investigation of the characteristics of L-cysteine as a prereducing reagent for As(V). We also report a method to determine total inorganic arsenic at low acid concentration with a flow-through batch hydride generator in which L-cysteine acts, not only as a prereducing agent, but also as a reagent which reduces interferences and also increases sensitivity.

Results and Discussion

L-Cysteine Enhances Signals

We have shown that acid concentration is critical in the determination of other elements by hydride generation^{33, 34}. Thus we have investigated the effect of acid concentrations

on the generation of arsine in the presence and absence of L-cysteine. In the absence of L-cysteine, the production of arsine, measured as peak height, increases steadily as the acid concentration increases, and reaches a plateau when the acid concentration reaches 0.08 - 0.10 M. In the presence of L-cysteine, on the other hand, arsine production reaches a maximum over a range of acid concentrations from 0.01 to 0.03 M. Over the best range of acid concentrations, the peak heights, where L-cysteine were used, are some 75% greater than peak heights obtained in 0.1 M acid in the absence of L-cysteine. No significant difference in behaviour was observed when nitric acid or hydrochloric acid was used as the acid medium.

Prereduction of As(V) by L-Cysteine

When studying the effect of L-cysteine on arsine generation from As(V), it was found that, over the range of acid concentrations from 0.01 - 0.02 M, no arsine was detected in the absence of L-cysteine. Measurement of the pH showed that, after 5 ml of the test solution reacted with 1 ml 2% m/V NaBH₄ solution (stabilized with 0.8% m/V NaOH), the final pH value was greater than 8. It was not surprising, therefore, that no arsine was released from the As(V) solution since As(V) has been reported to be reduced to arsine only in a strong acid medium.¹¹⁻¹² When L-cysteine solution was added to the arsenic(V) solution just before the NaBH₄ solution was added, almost no arsine was measured. If the solution was allowed to stand, the signal gradually increased with time. This phenomenon suggested that L-cysteine probably plays a role as a prereducing agent which reduces As(V) to As(III) and is itself oxidised to L-cystine. At room temperature and in 0.02M acid medium, the reduction of As(V) to As(III) was complete within 35, 60 and 135 min. when L-cysteine (1 g, 0.5 g and 0.25 g respectively) was added to 100 ml of 50 ng ml⁻¹ As(V) solution. When the solution in the 0.02M acid medium was heated in boiling water for only 5 minutes, As(V) was completely reduced to As(III). Heating for as long as 45 mins resulted in no arsenic loss. In addition, when prereduction was carried out in 1M acid with 0.5 g L-cysteine at room temperature, As(V) was completely reduced to As(III) within 5 min. Compared with the other systems tested, L-cysteine seems to be an excellent reagent for the prereduction of As(V).

Speciation

Since L-cysteine reduces As(V) to As(III) slowly at room temperature and at low acid concentration, it was felt that it might be possible to determine As(III) in the presence of As(V).

Thus, a solution containing As(III) and As(V) was injected into the generator; L-cysteine solution was then added, followed immediately by the NaBH₄ solution. In this way, only As(III) reacts to form arsine. A separate sample can be reduced with L-cysteine prior to the hydride generation step to give the total As(III) and As(V) concentration. Acid and NaBH₄ concentrations are critical factors for reducing As(V) interference in the determination of As(III). The best conditions for the determination of As(III) in the presence of As(V) are as follows: 1 ml of 2% m/V of L-cysteine is added to 5 ml of the solution of As(III) and As(V) in 0.01M HCl, immediately followed by addition of 1 ml of 0.5% m/V NaBH₄. Under these conditions, 2.5 µg As(V) did not interfere in the generation of arsine from 250 ng As(III).

Interference Studies

When studying interference, 1 ml of the interfering ion, at different concentrations, was directly added to the generator containing 5 ml of arsenic(III). The signals obtained in this way were compared with those where no interfering ion been added. Table 1 shows the interference of some transition elements and the interference-reducing effect of L-cysteine.

Table 1. Interference from Transition Elements and the Effect of L-Cysteine

Metal Ions	Concentration (µg ml ⁻¹)	Recovery (%)	
		No L-Cysteine ^a	With 0.5% m/V L-Cysteine ^b
Au(III)	0.2	95	102
	2	78	91
	20	8.0	77
Pt(IV)	0.2	100	100
	2	55	96
	20	2.0	92
Pd(II)	0.2	76.	92
	2	n.d. ^c	94
	20	-	85
	200	-	54.
Ag(I)	0.2	-	105
	2	87.	101
	20	42	95

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	200	-	87
Ni(II)	0.2	76	-
	2	11.5	98
	20	-	66
Co(II)	0.2	82	-
	2	25.8	-
	20	-	98
	200	-	64
Cu(II)	0.2	82	-
	2	67	-
	20	12.4	101
	200	-	96
Fe(III)	20	93	104
	200	-	99
Fe(II)	20	36	99
	200	-	99
	2000	-	91
Hg(II)	2	-	99
	20	95	103
	200	-	105
Mn(II)	20	91	99
	200	-	100
Zn(II)	20	65	99
	200	-	96
Cr(IV)	2	-	99
	20	101	102
	200	87	94
Cd(II)	20	96	102
	200	-	96
Mo(VI)	2	102	105
	20	189	98
	200	-	96

^a The concentration of As(III) was 50 ng ml⁻¹.

^b The concentration of As(III) was 125 ng ml⁻¹.

^c n.d. - not detected

Without L-cysteine, Pd, Pt, Au, Ag, Ni, Co, Cu, and Fe interfere with the hydride generation process and the interferences were more severe than in 5 M HCl medium,²⁷ which

agrees with the findings of Welz and Melcher.³⁰ Moreover, the interference resulted in a memory effect. Interfering ions, introduced to the generator in a determination, would depress the arsenic signal of the next determination even in the absence of interfering ions. This could be due to a residue of finely divided metal particles, precipitated on the generator, which was not completely removed during the cleaning. Interference in the generation of the hydride by finely divided metal has previously been reported by Welz and Melcher.³² Molybdenum was exceptional in that, in the absence of L-cysteine, enhanced recovery of arsenic was observed. The interference-free level of the above elements that could be tolerated was increased by one, two, and even three orders of magnitude, due to the presence of L-cysteine, and there was no observable memory effect. Compared to L-cysteine in 5 M HCl,²⁷ L-cysteine, even in 0.02 M HCl, reduced interferences more effectively from gold and palladium, though it was less effective in reducing interferences from cobalt and nickel. In addition, at the low acid concentrations used, L-cysteine, readily dissolves in solution and thus simplifies the method.

Table 2 shows that, except for tellurium and selenium, other hydride forming elements, at concentrations up to 20 $\mu\text{g ml}^{-1}$, have no influence on arsine generation in the system. It is also interesting to note that tellurium and selenium interfere more severely when L-cysteine is present than when it is absent.

Table 2. Interference of Hydride Forming Elements and the Effect of L-Cysteine

Ions	Concentration ($\mu\text{g ml}^{-1}$)	Recovery (%)	
		No L-Cysteine ^a	With 0.5% m/V L-Cysteine ^b
Bi(III)	2	96	102
	20	75	101
Ge(IV)	2	94	101
	20	95	102
Sb(III)	2	-	101
	20	100	101
Sn(II)	2	-	98
	20	101	99

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	200	-	100
Pb(II)	2	76	97
	20	56	100
Se(IV)	0.2	-	97
	2	106	94
	20	100	78
	200	63	7.7
Te(IV)	0.2	96	100
	2	100	53
	200	67	10.4

- The concentration of As(III) was 50 ppb.
- The concentration of As(III) was 125 ppb.

Detection Limit and Precision

The limit of the detection for As(III) (three times the standard deviation of the blank) was 0.62 ng ml^{-1} for a 5 ml sample. The relative standard deviation of ten determinations of 50 ng ml^{-1} As(III) was 1.1%.

Conclusion

The present study has shown that L-cysteine plays a three-fold role in the determination of total inorganic arsenic by means of hydride generation. First, it is an efficient prereducing agent compared with other prereductants. It can prereduce As(V) to As(III) completely in the low acid concentration required by the arsine generation reaction. Secondly, the arsine signal is increased by 75% in the presence of L-cysteine. Thirdly, interferences from foreign ions are significantly reduced due to the presence of L-cysteine. In addition, L-cysteine shifts the optimum acid concentration for arsine generation to 0.01 - 0.03 M, thus reducing the amount of hydrogen produced, which is beneficial in DCP-AES determination. The method can be used to determine trace concentrations of arsenic in difficult sample matrices.

References

1. Holak, W., *Anal. Chem.*, 1969, **41**, 1712.
2. Welz, B., *Chem. Br.*, 1986, **22**, 130-133.
3. Nakahara, T., *Prog. Anal. Atom. Spectrosc.*, 1983, **6**, 163-223.
4. Godden, R. and Thomerson, D.K., *Analyst*, 1980, **105**, 1137-1257.
5. Dedina, J., *Prog. Anal. Spectrosc.*, 1988, **11**, 251-260.
6. Riby, P.G., Haswell, S.J., and Grzeskowiak, R., *J. Anal. At. Spectrom.*, 1989, **4**, 181-184.
7. Huang, B., Zeng, X., Zhang, Z., and Liu, J., *Spectrochim Acta.*, Part B, 1988, **43B**, 381-389.
8. Ebdon, L. and Sparkes, S., *Microchem. J.*, 1987, **36**, 198-206.
9. Ek, P. and Hulden, S. U., *Talanta*, 1987, **34**, 495-502.
10. Boampong, C., Brindle, I.D., Ceccarelli-Ponzoni, C.M., *J. Anal. At. Spectrom.*, 1987, **2**, 1987-200.
11. Aggett, J. and Aspell, A.C., *Analyst*, 1976, **101**, 341-347.
12. Braman, R.S., Johnson, D.L., Foreback, C.C., Ammons, J.M., and Bricker, J.L., *Anal. Chem.*, 1977, **49**, 621-625.
13. Anderson, R., Thompson, M., and Culbard, E., *Analyst*, 1986, **111** 1143-1152; 1153-1158.
14. Van Cleuvenbergen, R.J.A., Van Mol, W.E., and Adams, F.C., *J. Anal. At. Spectrom.*, 1988, **3**, 169-176.
15. Welz, B. and Melcher, M., *Analyst*, 1984, **109**, 573-575.
16. Sinemus, H.W., Melcher, M., and Welz, B., *Atom. Spectrosc.*, 1981, **2**, 81-86.
17. Haring, B.J.A., Van Delft, W., and Bom, C.M., *Fresenius Z. Anal. Chem.*, 1982, **310**, 217-223.
18. Stephens, P., *Atomic Absorption Newsl.*, 1979, **18**, 118-120.

19. Terada, K., Matsumoto, and Inada, T., *Anal. Chim. Acta.*, 1984, **158**, 207-215.
20. Sun, S., and Xue, J., *Youkuangye*, 1986, **5**, 31-34.
21. Goulden, P.D. and Brooksbank, P., *Anal. Chem.*, 1974, **46**, 1431-1436.
22. Takahashi, Y., Ono, T., Yokoyama, T. and Taruntami, T., *Chinetsu*, 1987, **24**, 383-389.
23. Subramanian, K.S. and Meranger, J.C., *Anal. Chim. Acta.*, 1981, **124**, 131-142.
24. Chakraborti, D., De Jonghe, W., and Adam, F., *Anal. Chim. Acta.*, 1980, **120**, 121-127.
25. Chung, C., Iwamoto, E., Yamamoto, M., and Yamamoto, Y., *Spectrochim. Acta., Part B*, 1984, **39B**, 459-466.
26. Hamilton, T.W., Ellis, J., and Florence, T.M., *Anal. Chim. Acta.*, 1980, **119**, 125-233.
27. Boampong, C., Brindle, I.D., Le, X., Pidwerbersky, L., and Ceccarelli Ponzoni, C.M., *Anal. Chem.*, 1988, **60**, 1185-1188.
28. Smith, A.E., *Analyst*, 1975, **100**, 300-306.
29. Pierce, F.D. and Brown, H.R., *Anal. Chem.*, 1976, **48**, 693, 1977; **49**, 1417.
30. Welz, B. and Schubert-Jacobs, M., *J. Anal. At. Spectrom.*, 1986, **1**, 23-27.
31. Hershey, J.W. and Keliher, P.N., *Spectrochim Acta, Part B.*, 1986, **41B**, 713.
32. Welz, B. and Melcher, M., *Analyst*, 1984, **109**, 569-572.
33. Brindle, I.D., Le, X., and Li, X., *Analyst*, 1988, **113**, 1377-1381.
34. Brindle, I.D., Le X., *J. Anal. At. Spectrom.*, 1989, **4**, 227-232.
35. Brindle, I.D. and Le, X., *Anal. Chim. Acta*, 1990, **229**, 239-247.

VOLUME II

SESSION D

ANALYTICAL METHODS RESEARCH

POSTER PRESENTATIONS

EXPERT SYSTEMS IN ANALYTICAL CHEMISTRY. DESIGN OF A USER INTERFACE AND IMPLEMENTATION OF RULES FOR ACdiagnosis WITHIN ACexpert.

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Abstract This paper describes the application of expert system technology to analytical chemistry as part of the development of the ACexpert system. An expert system can be defined as a computer program that achieves a high level of performance in areas that otherwise require years of special education and training. In a rule based expert system knowledge is expressed in the form of conditional if-then rules. Here the main emphasis is on the power of reasoning, that is, the relations between facts rather than the facts themselves. The most widespread control applications of expert systems have been in diagnostics, in support of operators during disturbances (1,2).

DESIGN OF A USER INTERFACE FOR ACexpert

ACexpert is an expert system that deals with automated trace metal analysis by atomic absorption spectrometry (AAS). ACexpert is subdivided into individual expert system modules designed to perform specific tasks (3). The complexity and breadth of analytical chemistry means that ACexpert must be capable of interacting with several different modules, some rule based, some procedurally based, and some graphically based. To achieve this degree of flexibility, we have designed a general purpose user interface which can handle real-time problems, and at the same time will be able to provide access to any type of module.

Expert systems rely on data, these data will often be held in remote databases. As a result of regulations, large amounts of environmentally important analytical data are stored in databases. Over a number of years, these databases become so big that it is not possible to read these data without proper computer-aided "browsers". Because these database systems can be very large, decisions on the proper way to access the data are critical in the design of the ACexpert system. So, it is very important to add mathematical functions into the system which can convert the data into graphical representations. Based on all these requirements, the prototype of the ACexpert interface becomes very complex. After various tests, we decided to use Microsoft Windows 3.0 using ACTOR, an object oriented program, to help with the code writing. With these tools in hand, it is much simpler to design the interface. By adding different menus into different levels of windows, and by using the MOUSE, it becomes less difficult for the user to interact with the system and to handle real time problems. In our system, it is possible for the user to leave one window open, which could be showing a graphical display, and then open a second window to carry out calculations, the user can open third level windows to carry out rule based inferences. Also, it is possible to pass the results which are obtained from the calculation window to another window, and then to represent the data in the graphics window.

It is also very important to find a way to access a particular data file inside the database system. In order to solve this problem, a proper set of chemical knowledge is added to the system, so that the user can specify the type of data to be accessed within the database system. For example, if the user wants to open a data file, the system will first display a dialogue box which asks the user to fill in the necessary information, the system can then decide by itself which file the user is interested in and can display this data file in a display window. If the user does not know all the necessary information which is required by the system, then by filling in as much as he/she knows into the dialogue box, the system will output several data file names which are related to the information that the user has entered into the system. The user can then complete the choice from these files. On the other hand, if the user wants to add the data into the database, the system also displays a dialogue box which asks the user to enter the appropriate chemical information into it, the system then can decide the proper name and address for this particular file within the database.

IMPLEMENTATION OF RULES FOR ACdiagnosis

ACdiagnosis solves instrumental and chemical problems associated with flame atomic absorption analysis. We are using the expert system shell KDS-3 to develop our rule base. KDS-3 is an inductive expert system shell, that consists of a development component and a run time component. The development component allows information to be entered in the form of case histories broken into conditions and conclusions. The run time component permits distribution of the compiled version of the system to users. Because KDS-3 is an inductive expert system, the developer is required to specify knowledge in terms of conditions and conclusions. The relationship between each condition and conclusion is used to construct a set of rules. KDS-3 works in the sequence of facts...rules...knowledge base. This can be contrasted with subjective systems which evolve as rules...knowledge base. Facts are objective whereas explicitly entered rules are subjective since they consist of the opinions of one or more people. A computer with the proper software is far more capable of accurate and rapid logical analysis of a large number of facts than a human being.

The present module of ACdiagnosis is the second version of this expert system (4, 5). Here, we refer to the conditions as symptoms and the case conclusions as causes. We have determined the following symptoms:

1. Relative standard deviation values are high ($>5\%$); absorbance values are not precise.
2. Absorbance values are 50-80% of the expected values in the calibration graph.
3. Absorbance values are 20-40% of the expected values in the calibration graph.
4. Noisy absorption signal (observed in signal graphics).
5. Occasional pulse up or down in signal (observed from signal graphics).
6. Signal decays during aspiration (observed from signal graphics).
7. Pulsating signal (observed from signal graphics).

8. The calibration graph levels off at high concentrations.
9. The calibration curve is sigmoidal.
10. Change in absorption sensitivity between re-calibration.
11. Drift in baseline.
12. The flame has a ragged appearance.
13. A refractory element is present in the solution.
14. The samples are viscous.
15. The uptake rate is less than 5ml/min.
16. Fluctuating display while optimizing lamp.
17. Hollow cathode lamp on but no display while optimizing lamp.
18. Spectrometer is in single beam mode.
19. Integration time is less than 3 seconds.
20. You are using an oxidizing flame.
21. Low pressure in the fuel cylinder.
22. The burner is set above 8 on the vertical scale.
23. You are using nitrous oxide-acetylene flame.

The symptoms may be broadly classified into (a) instrumental conditions that existed before the sample analysis took place, and (b) problems encountered during the sample analysis. Since KDS gives only one answer at a time which solves only one problem, the user is expected to take the suggested corrective action and then consult the expert system for a second time for further advice, if needed. KDS would work better in a completely automated system wherein the system would carry out the required corrective action and proceed with the analysis. For instance, if the cause of the problem is an unstable lamp, the system would change the lamp and perform lamp optimization before proceeding with the analysis. The feature of KDS which allows the user to choose the most important symptom from a screen displaying all the possible symptoms is very useful. It allows the user to give a response to symptoms in an order better related to the specific problem. Each reappearance of the volunteer screen excludes from its display the symptoms which have been resolved directly or through inference since its last appearance.

The problem in writing rule based expert systems in analytical chemistry is that the chemical information must be encoded into rules. The knowledge (facts and rules) in KDS is represented in the form of a matrix consisting of case conclusions or causes (rows) and conditions or symptoms (columns). The rules are generated by inductive analysis of all the facts in the module.

A rule of the form "if subject (true) then predicate (true)" is generated when both the symptoms (the subject and the predicate) could be caused by the same problem. The following rules were generated because the subject and the predicate of each rule are associated with the same cause.

Rule: If low pressure in the fuel cylinder (is true) then drift in baseline (is true).

Rule: If the flame has a ragged appearance (is true) then the relative standard deviation values will be high ($>5\%$); absorbance values will not be precise (is true).

Rule: If low pressure in the fuel cylinder (is true) then noisy absorption signal will be observed in the signal graphics (is true).

A rule of the form "if subject (true) then predicate (false)" is generated when the subject and the predicate are not associated with the same problem, for example, "if relative standard deviation values are high ($>5\%$); absorbance values will not be precise (is true) then the burner is set above 8 on the vertical scale (is false)". This means that when the burner blocks the optical path no signal would be seen.

We are now familiar with building diagnostic expert systems and have built one for troubleshooting in gas chromatography. We realize the importance of a friendly user interface and have started work on designing graphical images that will replace textual forms of symptoms.

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REFERENCES

1. R. G. Bowerman, and D. E. Glover in *Putting Expert Systems into Practice*, Van Nostrand Reinhold Co., New York, 1988, 1-38.
2. D. A. Waterman, *A Guide to Expert Systems*, Addison-Wesley Publishing Company, California, 1986, 12-79.
3. W. R. Browett, and M. J. Stillman, *Prog. analyst Spectrosc.*, 1989, 12, 73-110.
4. W. R. Browett, T. A. Cox, and, M. J. Stillman in *Expert System Applications in Chemistry*, B. A. Hohne, and T. H. Pierce, American Chemical Society, Washington, 1989, 210-235.
5. M. J. Stillman, S. Lahiri, Q. Zhu, *Proceedings of the Technology Transfer Conference*, 1990.

DEVELOPMENT OF A TURN-KEY SYSTEM FOR HAZARDOUS WASTES ANALYSIS

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SUMMARY

A turn-key hazardous wastes analysis system has been developed using Fourier transform attenuated total reflectance infrared spectrometry, artificial intelligence assisted library searching and an automated infrared interpreter. Both the library searching and the infrared interpreter take advantage of the portability, the computing power and the mass data storage available for PC systems and is demonstrated to be a cost effective tool to assure consistent data interpretation. This turn-key system has a 10 nanogram detection limit and provides fast sample turn-around-time. The possibility of direct sample analysis without any clean-up process is demonstrated. Preliminary results from this developmental work indicate the possible improvement of sample throughput by as much as 300%.

INTRODUCTION

This automated infrared interpreter was developed on an IBM personal computer (PC) running under the Microsoft disk operating system (DOS). Based on the original Merck Sharp & Dhome Research Laboratory Program for the Analysis of Infrared Spectra (PAIRS) (1,2), this infrared interpreter, PC PAIRS*, is capable of analyzing infrared spectra measured with a wide variety of spectrophotometers. Modifications have been made to PAIRS to enable the application of both artificial

intelligence and library searching. Furthermore, a new algorithm has been devised to combine the results from the library searching and the PAIRS program to obtain high confidence level interpretational data. Major functionalities of the PC PAIRS⁺ are illustrated in Figure 1.

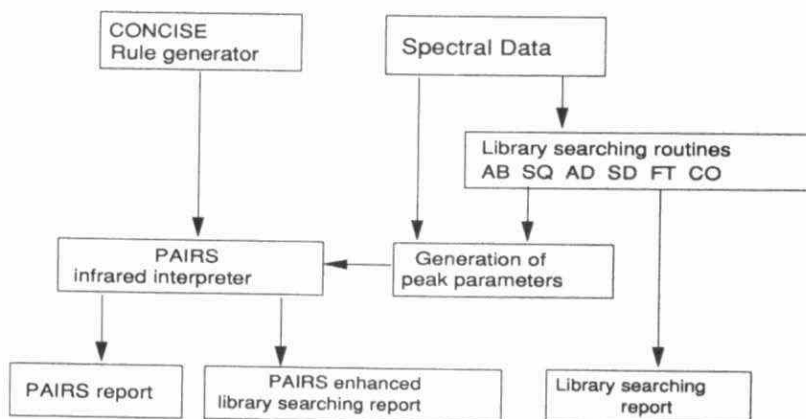


Figure 1. Functionalities of PC PAIRS+

All software was developed on a Magus Data Technology (Richmond Hill, Ontario) 80386/80387 IBM DOS PC running at a clock speed of 20 MHz. The

original PAIRS and the infrared interpretation rule generator, the Computer Oriented Notation Concerning Infrared Spectral Evaluation (CONCISE) (3,4) language, were obtained from the Quantum Chemistry Program Exchange (Bloomington, Indiana, Catalog # QCPE 426). The programs were downloaded into the PC via a RS-232 line from a VAX 780 system. Both programs were modified and converted to standard Ryan McFarland FORTRAN (Phoenix Computer Products, Norwood, MA) conventions, compiled and run on the same PC.

The library searching subprogram used five search algorithms. They are: absolute difference (AB), square of absolute difference (SQ), absolute difference of first derivative (AD), square of difference of first derivative (SD) and time domain cross correlation (FT). One additional algorithm was developed as part of this project to combine the library searching results from the first five algorithms, the combined algorithm (CO).

EXPERIMENTAL

A. Chemicals and Method of Analysis. A total of 67 oil and grease samples were measured in this work. These samples are standards of the most commonly encountered petroleum hydrocarbons and greases in the province of Ontario. A Barnes (SpectraTech Inc., Stamford, CT) micro circle cell accessory was used to measure the attenuated total reflectance (ATR) spectra of the samples. These spectra then formed the MOE Oil & Grease Library.

Several ATR infrared spectra were generated to test the software and the Oil & Grease library. Typically, about 2 ml of oil samples were used to spike one litre of tap water. Using the standard MOE method for the solvent extractable (5) the oils was extracted from the water sample using dichloromethane. Upon evaporation of the solvent the infrared spectrum of the residue was measured

B. Instrumentation. Either a BOMEM MB-100 (Quebec, Quebec) or a Nicolet 5SX (Madison, WI) Fourier transform infrared (FT-IR) spectrometer was used to measure the spectra. An optical retardation of 0.25 cm was used to signal average 100 single sided interferograms with a resolution of 2 cm^{-1} . The BOMEM FT-IR used an IBM DOS PC computer for the data collection and manipulation. For the Nicolet 5SX FT-IR, a Nicolet 620 data system was used to serve the purposes. Spectra measured with the BOMEM FT-IR were used without any change. For spectra measured on the Nicolet FT-IR a NICOMPC communication software (Nicolet Inc., Madison, WI) was used to download the spectra into the PC via a RS-232 line. The downloaded spectra were then used to create the spectral library.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the process employed by PC PAIRS⁺ in the evaluation of unknown spectra and report generation. Library searching was used for the positive identification of unknowns. In order to minimize the effect of noise and baseline problems of the infrared spectrum, results from all five library searching

algorithms (AB, SQ, AD, SD, CO) were combined to determine the best match for the unknown. Table 1 illustrates a typical library searching report from this turn-key system. The test sample used was IOSOL 1520, a common paint thinner used for the oil based paint. The library searching routine was set to list the five best matches from each individual routine. From Table 1, the AB and the SQ algorithms fail to identify the unknown from the Oil & Grease library. The CO method, on the other hand, successfully identified this unknown and many others, supporting its use as the method of choice for the library searching.

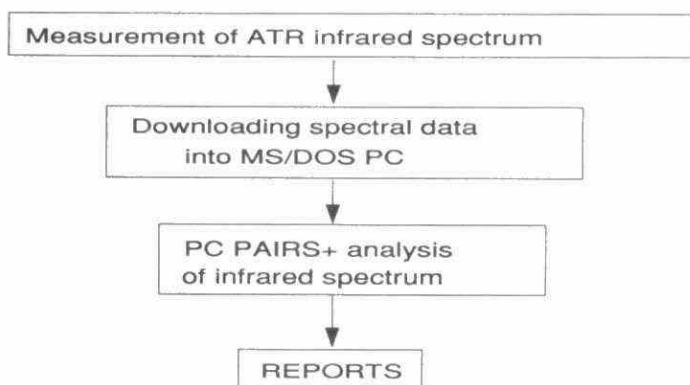


Figure 2. Procedures for a typical unknown sample analysis using the turn-key system.

Although the oil library with the five search algorithms have been successful for the identification of many routine sample analysis, we have encountered some situations where PAIRS⁺ proved to be superior. To illustrate this we added digital noise to a spectrum of Turbo A-1 oil to simulate the spectrum of an unknown organic extracted with dichloromethane. This spectrum was then searched through our oil library using CO algorithm. The result is shown in Figure 3. From this Figure, it is clear that all three matches and the test spectrum have identical spectra which makes the identification of the test spectrum from the library searching results impossible. Using PAIRS⁺, although interpretational results from the infrared interpreter indicated the presence of methyl and methylene group in the unknown and in all three matches, the probability order for the "functional groups" identifies the match #1 as the correct identification. These results are listed in Table 2. By comparing the probabilities obtained for match #1 with those obtained for matches #2 and #3 one can conclude that only match #1 is the correct answer.

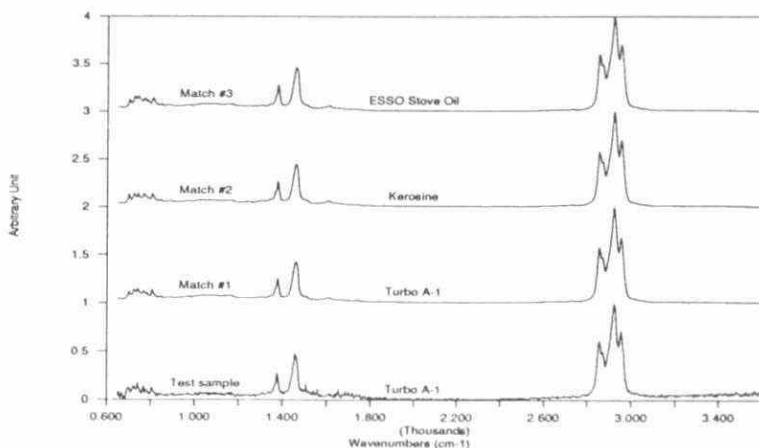


Figure 3. Library searching results for the test sample using the CO method. The close resemblance between the unknown and the three matching spectra complicates the task of positive identification requiring.

CONCLUSIONS

A turn-key system has been developed to utilize artificial intelligence and the positive identification capability of the library searching. The CO algorithm which combines results from five different library searching routines can obtain high quality library searching data. The typical analysis time of this turn-key system, including the data entry, the library searching and the final PAIRS' interpretation, is about five minutes per sample. PC PAIRS* not only increases the sample throughput of routine sample identification in the laboratory but also standardizes the procedure of infrared data interpretation. Current system is with an enhanced user interface and takes advantage of the ready access and user friendly nature of PC computer systems, therefore, can be an invaluable training system in the laboratory.

REFERENCES

1. Woodruff, H.B. and Munk, M.E., Analytica Chimica Acta, **95**, 13 (1977).
2. Woodruff, H.B. and Smith, G.M., Anal. Chem., **52**, 2321 (1980).
3. Woodruff, H.B. and Smith, G.M., Analytica Chimica Acta, **133**, 545 (1981).
4. Tomellini, S.A., Hartwick, R.A., Stevenson, J.M. and Woodruff, H.B., Analytica Chimica Acta, **162**, 227 (1984).
5. Ontario Ministry of the Environment Method SXT-E3201A.1, Rexdale, Ontario, Canada.

Table 1. Typical PC PAIRS+ Library Searching Report

The sample spectrum is: IOSOL 1520

The reference library is: >>>> The Oil Library <<<<<

The Library Search Result

(The FT Method)

- * Match #1 with probability of >>>>>>> 0.020430 <<<<<<<<<:
File # 35: IOSOL 1520, TRACE ORGANICS
- * Match #2 with probability of >>>>>>> 0.024283 <<<<<<<<<:
File # 19: ESSO REGULAR GASOLINE, TRACE ORGANICS
- * Match #3 with probability of >>>>>>> 0.026579 <<<<<<<<<:
File # 21: ISOPAR 'M', TRACE ORGANICS
- * Match #4 with probability of >>>>>>> 0.029905 <<<<<<<<<:
File # 32: ISOPAR 'K', TRACE ORGANICS
- * Match #5 with probability of >>>>>>> 0.052817 <<<<<<<<<:
File # 4: DISTILLED ISOPAR H, TRACE ORGANICS

The Library Search Result

(The AB Method)

- * Match #1 with probability of >>>>>>> 27.904972 <<<<<<<<<:
File # 16: IOSOL 1125, TRACE ORGANICS
- * Match #2 with probability of >>>>>>> 30.336798 <<<<<<<<<:
File # 32: ISOPAR 'K', TRACE ORGANICS
- * Match #3 with probability of >>>>>>> 30.400099 <<<<<<<<<:
File # 21: ISOPAR 'M', TRACE ORGANICS
- * Match #4 with probability of >>>>>>> 32.325081 <<<<<<<<<:
File # 53: TURBO FUEL, TRACE ORGANICS
- * Match #5 with probability of >>>>>>> 32.441692 <<<<<<<<<:
File # 27: IOSOL 2024, TRACE ORGANICS

The Library Search Result

(The AD Method)

- * Match #1 with probability of >>>>>>> 2.182141 <<<<<<<<<:
File # 35: IOSOL 1520, TRACE ORGANICS
- * Match #2 with probability of >>>>>>> 3.216939 <<<<<<<<<:
File # 32: ISOPAR 'K', TRACE ORGANICS
- * Match #3 with probability of >>>>>>> 3.284418 <<<<<<<<<:
File # 21: ISOPAR 'M', TRACE ORGANICS
- * Match #4 with probability of >>>>>>> 4.126999 <<<<<<<<<:
File # 16: IOSOL 1125, TRACE ORGANICS
- * Match #5 with probability of >>>>>>> 4.243579 <<<<<<<<<:
File # 24: VARSOL 3135, TRACE ORGANICS

The Library Search Result

(The SD Method)

Table 2. Typical report from the automated infrared interpreter

Spectral data summary for: Turbo A-1

The solvent is: neat

No empirical formula given

There are 8 peaks			
Line	Width	Intensity	Location
1	sharp	3	727
2	average	1	1367
3	sharp	3	1379
4	average	4	1460
5	sharp	4	1464
6	average	5	2873
7	average	8	2925
8	average	10	2956

Printout is sorted by probability:

Group name	Probability
1) METHYL	0.85
2) METHYLENE	0.49
3) AROMATIC	0.05
4) ACID	0.05
5) HETEROAROMATIC	0.01
6) PYRIDYL	0.01
7) PYRAZYL	0.01
8) PYRIMIDYL	0.01
9) PURINE	0.01
10) INDOLE	0.01

Interpretation for library match # 1.....

Spectral data summary for: Turbo A-1, TRACE ORGANICS

The solvent is: neat

No empirical formula given

There are 7 peaks			
Line	Width	Intensity	Location
1	average	2	727
2	average	2	1377
3	average	4	1456
4	average	5	2856
5	sharp	6	2870
6	average	10	2922
7	sharp	9	2952

Printout is sorted by probability:

Group name	Probability
1) METHYLENE	0.71
2) METHYL	0.60
3) ACID	0.05
4) PYRROLE	0.00
5) FURAN	0.00
6) THIOPHENE	0.00

7) AROMATIC	0.00
8) AROM-MONOSUBST	0.00
9) Z1	0.00
10) AROM-1.2-SUBST	0.00

Interpretation for library match # 2.....

Spectral data summary for: Kerosine, TRACE ORGANICS

The solvent is: neat

No empirical formula given

There are		24 peaks	
Line	Width	Intensity	Location
1	sharp	1	729
2	sharp	1	739
3	sharp	1	771
4	sharp	1	918
5	sharp	1	964
6	sharp	1	980
7	sharp	1	1007
8	sharp	1	1043
9	sharp	1	1055
10	sharp	1	1063
11	sharp	1	1066
12	sharp	1	1074
13	sharp	1	1090
14	sharp	1	1097
15	sharp	1	1124
16	sharp	1	1151
17	sharp	1	1169
18	sharp	1	1340
19	sharp	3	1365
20	average	4	1379
21	average	5	1464
22	average	6	2873
23	broad	7	2927
24	average	10	2956

Printout is sorted by probability:

Group name	Probability
1) METHYL	0.88
2) ACID	0.75
3) METHYL-GEMDI	0.55
4) KETAL	0.45
5) AMINE	0.40
6) AMINE-TERTIARY	0.40
7) ACETAL	0.40
8) NH3+	0.25
9) MERCAPTAN	0.25
10) METHYLENE	0.22
11) AROMATIC	0.05
12) HETEROAROMATIC	0.01
13) PYRIDYL	0.01
14) PYRAZYL	0.01

15) PYRIMIDYL	0.01
16) PURINE	0.01
17) INDOLE	0.01
18) PYRROLE	0.00
19) FURAN	0.00
20) THIOPHENE	0.00

Interpretation for library match # 3.....

Spectral data summary for: ESSO Stove Oil, TRACE ORGANICS

The solvent is: neat

No empirical formula given

There are 22 peaks

Line	Width	Intensity	Location
1	average	1	739
2	sharp	1	773
3	sharp	1	918
4	sharp	1	964
5	sharp	1	1007
6	sharp	1	1032
7	sharp	1	1038
8	sharp	1	1045
9	sharp	1	1055
10	sharp	1	1059
11	sharp	1	1068
12	sharp	1	1082
13	sharp	1	1103
14	sharp	1	1122
15	sharp	1	1151
16	sharp	1	1169
17	sharp	3	1365
18	average	4	1379
19	average	5	1460
20	average	6	2871
21	sharp	7	2927
22	average	10	2956

Printout is sorted by probability:

Group name	Probability
1) METHYL	0.93
2) ACETAL	0.84
3) METHYL-GEMDI	0.55
4) KETAL	0.52
5) METHYLENE	0.49
6) AMINE	0.40
7) AMINE-TERTIARY	0.40
8) AROMATIC	0.05
9) ACID	0.05
10) HETEROAROMATIC	0.01
11) PYRIDYL	0.01
12) PYRAZYL	0.01
13) PYRIMIDYL	0.01
14) PURINE	0.01
15) INDOLE	0.01

Study of the Effect of Solvent and Stationary Phase on the Chromatographic Behaviour of PAHs

Ian D. Brindle and Xing-fang Li

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St. Catharines, Ontario L2S 3A1

Preliminary observation has shown that peak shapes of PAHs on capillary GC/MS were influenced by the initial temperature used¹. Fronting was observed in several early-eluting peaks of 16 priority PAHs in toluene when the initial temperature was lower than 110 °C. When the initial temperature was higher than 130 °C, peak tailing occurred. To find more detailed information, the effect of initial temperature on peak shape was further investigated and proved to be more severe when initial temperature is very low. The chromatographic behaviour of PAHs on GC was found to be strongly influenced by the properties of the solvent used for injection and the stationary phase. An explanation is suggested based on these observations. Interactions between various factors, such as initial temperature, injection volume, solvent, and stationary were also studied. Since previous results suggests that better sensitivities of PAHs can be obtained with a high boiling point solvent, a wide range of solvents with boiling points from 40 °C for dichloromethane to 151 °C for nonane and even to 215 °C for dodecane. The best response was found with nonane as solvent.

Effect of initial temperature on peak shape

A series of experiments were performed with the initial temperature varied from 88 °C to 258 °C. GC/MS peak profiles were obtained when a 2 µl solution of 2 µg ml⁻¹ of each PAH in p-xylene was injected at an initial temperature of (a) 88 °C, (b) 128 °C, and (c) 138 °C. Peak shape varies significantly with the initial column temperature. When the initial temperature is 138 °C, a chromatogram with symmetric GC peaks is obtained. However, with the decrease of the initial temperature, the effect of fronting and splitting of the PAH peaks became greater. Fronting of the GC peaks appears at the initial column temperature of 128 °C and each peak is split into two when the initial temperature was 88 °C. Similar effects were observed when PAHs were made up in other aromatic solvents, such as benzene and toluene. This splitting phenomenon was mainly observed for the first 10 peaks of the 16 PAHs.

In order further to study the dependence of peak profiles on initial temperature, a number of experiments were carried out under different initial temperatures, while other parameters were kept constant. Peak shapes of each of 16 PAHs in different solvents were recorded at different initial temperatures. The relation between peak shape of each PAH and initial temperature is illustrated in Figures 1-4. Figures 1, 2, 3, and 4 were obtained when toluene, p-xylene, isooctane and nonane were used as solvents. The boiling points on the X axis correspond to each PAH determined. Peaks except 13, 15 and 16 are presented in these figures. The upper curve in Figures 1-4 shows the maximum initial temperatures, above which peaks start tailing. The lower curve shows the minimum initial temperature, below which fronting of peaks is observed. These two curves divide the space into three regions. Within the bottom region, under the minimum initial temperature curve, fronting or split peaks occurred. Tailing peaks were observed in the top region above the maximum

initial temperature curve. In the middle region, between the two curves, very good symmetrical peaks were obtained, indicating the optimum initial temperature with regard to peak shape. As shown in the Figures, the optimum initial temperature varies with different PAHs. This optimum range generally increases with the increase of boiling points of PAHs. Thus the early eluting PAH peaks have narrow critical ranges, whereas the late eluting PAHs give much wider optimum range. Below the minimum initial temperature curve, GC peaks begin to exhibit fronting and the fronting or splitting of peaks worsens as the temperature decreases. Similarly, tailing of the peak gradually occurs above the maximum initial temperature shown in the Figures, and becomes more severe when the initial temperature increases more over the maximum initial temperature.

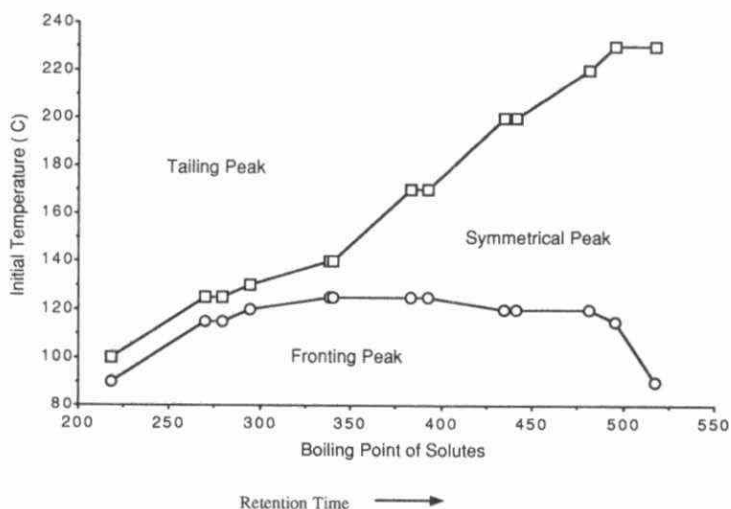


Figure 1. Effect of Initial Temperature on Peak Shape of 16 PAHs in Toluene

Conditions: temperature program one; crosslinked methyl silicone column;

injection volume: 2 μl of 2 $\mu\text{g ml}^{-1}$ PAHs in toluene.

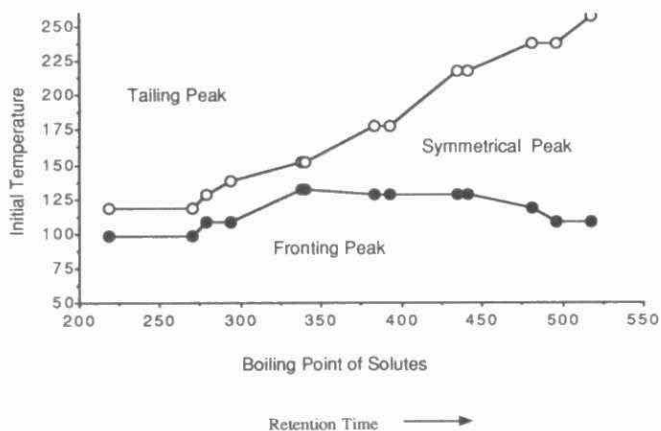


Figure 2. Effect of Initial Temperature on Peak Shape of 16 PAHs in p-Xylene

Conditions: temperature program two; others see Figure 1.

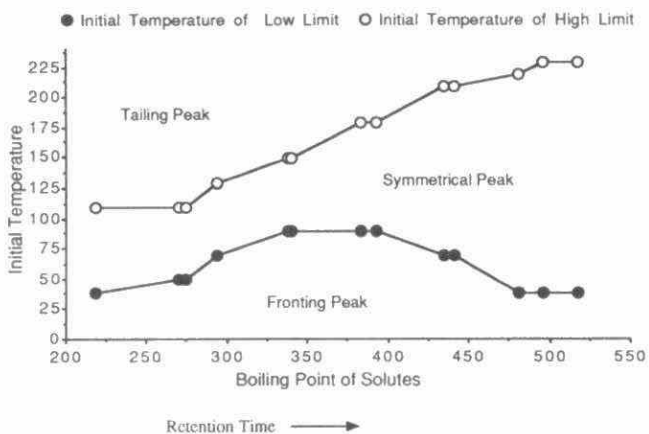


Figure 3. Effect of Initial Temperature on Peak Shape of 16 PAHs in Isooctane

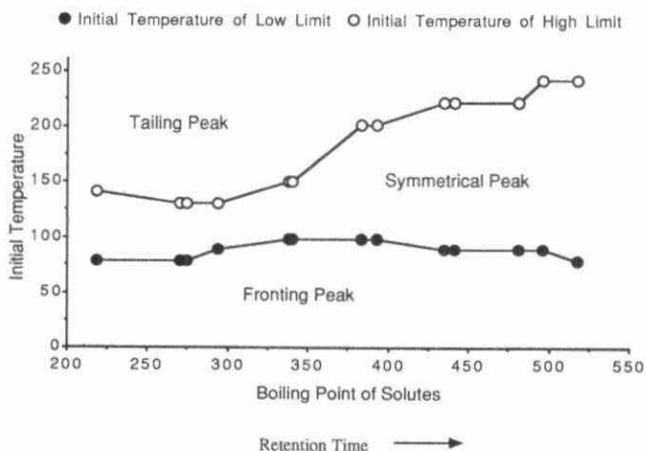


Figure 4. Effect of Initial Temperature on Peak Shape of 16 PAHs in Nonane

The optimum initial temperature range also depends on the solvent used for the injection of PAHs. Comparing figure 1-4, we can see that the ranges of initial temperature for symmetrical peaks are larger in alkane solvents such as isooctane and nonane than that in aromatic solvents like toluene and p-xylene. The optimum ranges of initial temperature for symmetrical peaks 2 and 3, for example, are approximately 110 to 120 °C in toluene, 108 to 138 °C in p-xylene, 49 to 109 °C in isooctane, and 81 to 141 °C in nonane as illustrated in the above figures.

Reference:

1. Ian D. Brindle and Xing-fang Li, *Journal of Chromatography*, 1990, **498**, 11-24.

MONITORING AMBIENT AIR VOCs USING CRYOGENIC AND ADSORBENT TRAP A CRITICAL EVALUATION

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INTRODUCTION

Analysis of ambient air volatile organic compounds (VOCs) is a complex task. This is due primarily to: 1. the wide variety of compounds of interest and 2. an ineffective means of analysis. The US EPA suggested a core set of three methods for sampling and analysis of ambient air VOCs (1). For the complete analysis of VOCs having boiling points from -10 to 200°C, the method suggested the use of a cryogenic analytical trap. This has been the method of choice, because it allows for the complete analysis of VOCs in a once-through type of operation. Of course, the use of a liquid N₂ cooled trap would imply the limited mobility of the system. This cryogenic trap also implies that atmospheric water vapor would be frozen in the trap, thus, clogging the trap and finally be desorbed into the GC. Therefore, creating many retention indices shift problems during the separation. In addition, with the equipment being operated at two extreme of temperatures, i.e., from -196 to 220°C, it would always be a major contributing factor to the downtime.

One alternative to the cryogenic analytical trap is an adsorbent packed analytical trap. The advent of a new variety of adsorbents grants us the capability of adsorbing/desorbing compounds with a fairly wide range of boiling points. We

have therefore evaluated in this work, the validity of using an adsorbent analytical trap to do the analysis on the VOCs. Presented in this paper is the description of the objectives and results obtained from this work. Preliminary results were obtained using two adsorbent packed analytical traps. QA/QC data will be presented to demonstrate the advantages/disadvantages of using an adsorbent analytical trap for the VOC analysis.

EXPERIMENT

The adsorbent based analytical trap VOC thermal desorption / gas chromatograph / mass spectrometer system (TD/GC/MS) consists of a Tekmar LSC2000 thermodesorber (Cincinnati, OH), a Tekmar 4210 autosampler, a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and a Hewlett-Packard 300 series data station. The cryogenic trap VOC TD/GC/MS system consists of a Tekmar 5010 thermodesorber (Cincinnati, OH), a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and an Intel 80386/80387 based data station. Figure 1 illustrates a general block diagram of the two systems.

Two adsorbent analytical traps were used to concentrate the VOCs for the subsequent GC/MS analysis. Both analytical traps were obtained from Supelco Canada (Oakville, Ontario). The first one is a standard adsorbent trap (Supelco Cata. # 2-0321). The second analytical trap is a proprietary trap (2), courtesy of

Supelco Canada. Spiking mixtures were prepared using a modified gas mixing chamber (Lasale Glass, Barrie, Ontario). All data presented was obtained from both within run and between run experiments.

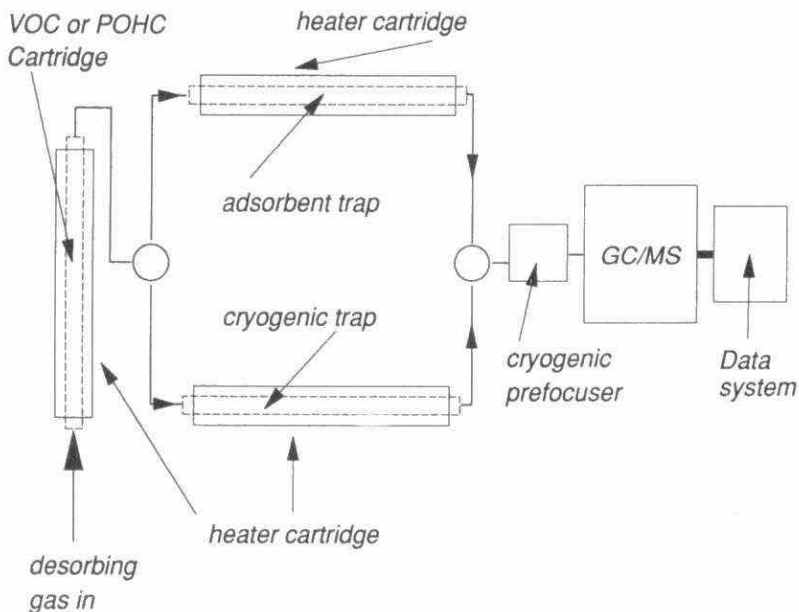


Figure 1. Block diagram of cryogenic and adsorbent based TD/GC/MS systems for the ambient air VOC analysis.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the total ion chromatogram (TIC) obtained from the cryo-

genic TD/GC/MS system. Figure 3 illustrates the TIC obtained from the adsorbent based TD/GC/MS system. Table 1 illustrates the QA/QC evaluation data obtained from the proprietary adsorbent trap TD/GC/MS system. Standard deviation data obtained from the standard adsorbent trap was too high to be useful. Table 2 illustrates preliminarily QA/QC data obtained from the cryogenic analytical trap TD/GC/MS system.

It is peculiar to note that we could not obtain useful data from the standard trap (Supelco cata.# 2-0321) which was capable of trapping the low boiling point volatile organic compounds under the purge and trap GC operation. The new trap (2) would allow us to trap the low boiling point VOCs in the TD/GC/MS system. Future studies are required to address this question.

CONCLUSION

We have demonstrated that applying adsorbent based TD/GC/MS system for the ambient air VOC analysis is feasible. Possibility of eliminate a cryogenic trap for the TD/GC/MS system offers a cost effective approach for the VOC analysis. Problems from liquid nitrogen related instrument downtime would have been eliminated, achieving a constant, maximized sample throughput.

REFERENCES

1. "Compendium of methods for the determination of toxic organic compounds in ambient air", R.M.Riggin, Battelle-Columbus Laboratories, Columbus, Ohio.
2. Robert Belardi, Supelco Canada, Oakville, Ontario, private communication.

TABLE 1. QA/QC DATA OBTAINED FROM AN ADSORBENT ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*	
		within	between
METHYL CHLORIDE (-23)	103.3	21.4	34.61
VINYL CHLORIDE (-13.9)	136.8	16.22	43.40
1,3-BUTADIENE (-4.5)	97.5	17.41	47.72
1,1-DICHLOROETHANE (31.9)	182.7	19.02	43.98
TRICHLOROMETHANE (61)	222.6	29.3	32.83
BENZENE (80)	131.8	33.03	42.78
BROMODICHLOROMETHANE (90)	295.65	31.07	43.04
TOLUENE (110)	129.9	23.62	34.11
1,2-DIBROMOMETHANE (131)	405.11	30.48	47.12
CHLOROBENZENE (131)	166.11	21.05	36.55
1,2-DICHLOROBENZENE (180)	195.0	9.48	18.48
NAPHTHALENE (217)	174.3	16.61	14.57

* Presented in $\pm\%$ to the spiked amount. The within run and between run data was obtained from 11 and 23 experiments, respectively.

TABLE 2. QA/QC DATA OBTAINED FROM AN CRYOGENIC ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*
METHYL CHLORIDE (-23)	103.3	N/A
VINYL CHLORIDE (-13.9)	136.8	N/A
1,3-BUTADIENE (-4.5)	97.5	11.32
1,1-DICHLOROETHANE (31.9)	182.7	8.80
TRICHLOROMETHANE (61)	222.6	9.41
BENZENE (80)	131.8	10.2
BROMODICHLOROMETHANE (90)	295.7	18.9
TOLUENE (110)	129.9	6.73
1,2-DIBROMOMETHANE (131)	405.2	N/A
CHLOROBENZENE (131)	166.1	4.39
1,2-DICHLOROBENZENE (180)	195.0	4.81
NAPHTHALENE (217)	174.3	8.23

* Presented in $\pm\%$ to the spiked amount. Data obtained from 8 within run experiemnt.

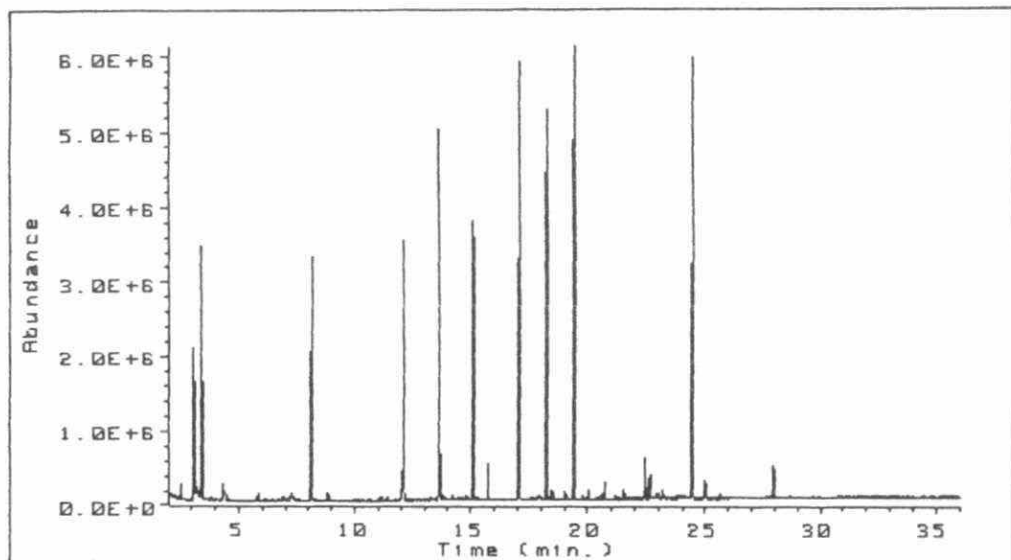
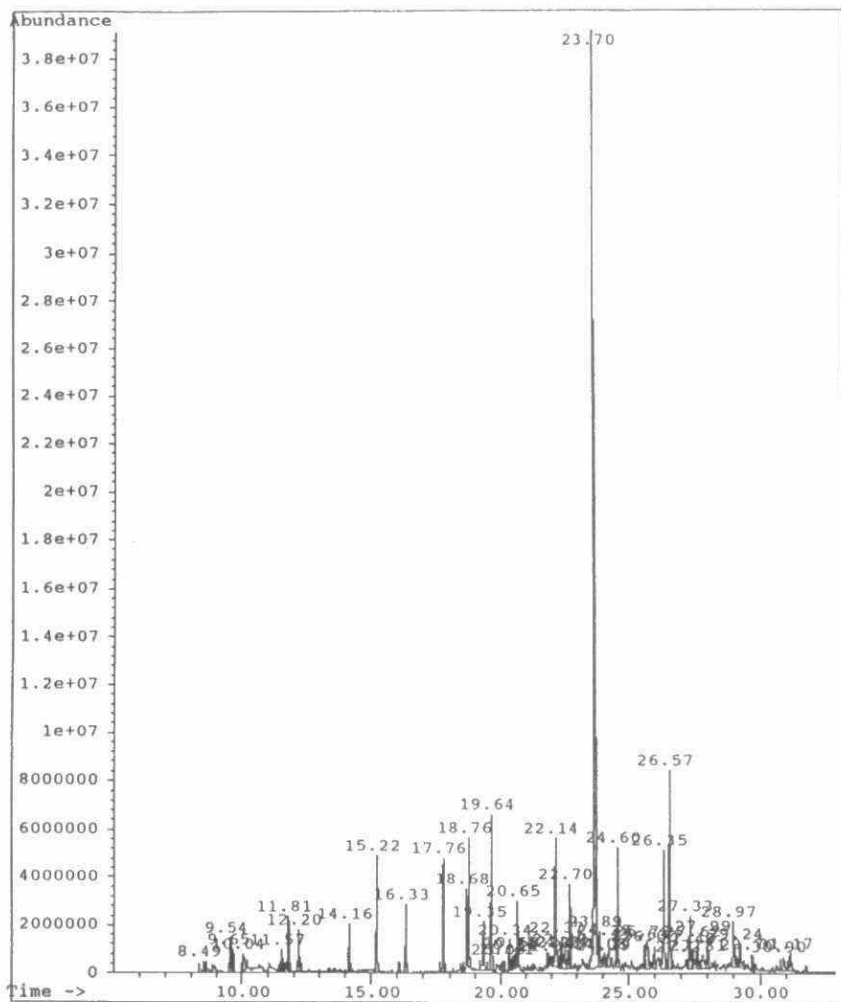


Figure 2: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system.

Figure 3: Total Ion Chromatogram obtained from the Ambient Air
 VOC TD/GC/MS system using Cryogenic Analytical Trap.



ADAPTATION OF WATER PRECONCENTRATION TECHNIQUES DEVELOPED FOR PCDD ANALYSIS TO OTHER TARGET ORGANIC POLLUTANTS. C. Shewchuk*, L.J. Brownlee, C. Bernard and B.R. Hollebone, Chemistry Department, Carleton University, Ottawa, Ontario, K1S 5B6.

INTRODUCTION

These laboratories, in conjunction with the Ontario Ministry of Environment, have developed a sampling unit capable of preconcentrating water for ultratrace detection of PCDDs as part of a water quality monitoring program for raw and treated drinking water¹.

The automatic preconcentration sampler (APS) incorporates both filtration and adsorption technology. The adsorption technology utilizes a macroreticular resin (XAD-2) column, in duplicate, for which sampling conditions and elution and detection procedures have been established to permit recovery and analysis of dioxins at the ppq level². The filter system is based on setting the distinction between dissolved and insoluble particles at 0.45 μm . The duplicate filter systems each consist of 2 tubular filters placed in series to accommodate approximately 30 L of 5-10 NTU water and trapping $>0.3 \mu\text{m}$ particles at 98% retention.

It is essential to incorporate filtration in a sampling unit since natural water contains suspended mineral particles, coated with colloidal metal oxides and humic acids, which adsorb and transport significant amounts of organic contaminants. In conventional water sampling techniques, using only adsorption media, the presence of particulate matter interferes with the accurate recovery and quantitation of the analytes. The APS overcomes this loss factor by preconcentrating organics using analytical filtration and resin technology in series.

Calibration experiments to determine dioxin recoveries using the APS showed that all dioxin congeners tested were located on the filter, with no detectable levels on the XAD-2 resin¹. Other laboratories, when analyzing river water for PCBs, have found that a substantial portion of the organochlorines from the water sample was located on the filtered sediment^(3,4). Thus, in its present configuration, the APS can be adapted to the detection of two types of organic contaminants; those which are adsorbed on particulates and retained by the filter, and those which remain dissolved in the aqueous phase and adsorbed on the XAD column.

In order to develop a more comprehensive protocol for the APS unit, the behaviour of eight compounds selected from the Ontario Ministry of the Environment priority pollutant list have been studied in the presence of a representative clay suspension.

EXPERIMENTAL

The compounds chosen for this study include two polyaromatic hydrocarbons, benzoperylene and anthracene, and five organochlorines, PCBs, 1,2,4-trichlorobenzene, octachlorostyrene, 2,4,5-trichlorotoluene, lindane and Mirex. These compounds vary in aromaticity, molecular weight, and degree of chlorination since these characteristics may influence the distribution behaviour.

APS Testing

The first run consisted of 40 L of distilled water only, passed through filters and columns, to observe background noise. The remaining experiments were performed using a 40 L spike solution of the target organics in distilled/deionized water, pumped at flow rate of 200 mL/min and a concentration of 10 ng/L, through the sampler (a total of 400 ng of each target compound was passed through the sampler). One run involved passing the spike solution through the column only so it could be evaluated without the interference of the filters. The behaviour of target organics was then studied as a function of turbidity. Illite solutions at turbidities of 0, 0.1, 0.5, 1, 5 and 10 NTU were passed through the filters and columns.

In situ Extraction Apparatus

The current procedure for extraction of organic analytes from a solid matrix such as a filter or soil sample is soxhlet extraction.

To adapt this process to Balston or cartridge filters there are several problems. To accommodate the filter size, a soxhlet apparatus must have a sample chamber of 1500 mL or 5000 mL which can cost \$700.00 or \$1200.00 respectively. An apparatus of this size is awkward to clean and handle on a routine basis.

In addition, in order to use a traditional Soxhlet apparatus, the filter must be transferred from the filter housing to the apparatus without compromising the analytical integrity of the filter or contaminating the worker by exposure to toxic chemicals on the filter.

The objective of this part of the study was to examine the feasibility of an *in situ* Soxhlet extractor using the filter housing as the sampler compartment of the extraction vessel.

A prototype has been constructed. The main feature consists of a glass adapter which connects the condenser to the round bottom flask. This adapter contains the syphon and a small built-in funnel that is designed to collect the condensed solvent and carry it to the filter housing. The glass tube extending from this funnel is connected to a flexible stainless steel tube which ends in a Swagelok connector used to join the assembly to the filter housing. Through this connection the solvent enters the housing. The solvent exits at the bottom of the housing through an identical connection. After the stainless steel tube joins the glass tube, the glass makes a ninety degree turn upwards to form the syphon.

There was no time in the study to test this apparatus for efficiency of extraction.

RESULTS AND DISCUSSION

Method tests of filter extraction and extract preparation for instrument analysis were performed on all spike compounds to determine efficiency of the procedure for recovery of analytes. The values are shown in table 1. Column extraction recoveries were not evaluated in this study since they have been done in other work⁵.

The most volatile of the compounds, 1,2,4-trichlorobenzene, was not recovered well, probably due to evaporative losses. Moderately volatile compounds such as 2,4,5-trichlorotoluene

and anthracene also showed some evaporation loss. Benzoperylene was not recovered at all probably because this heavy compound remained on the glassware during the work up stage. It would appear as though the recovery of analytes from the filters suffered similar losses as the sample work up, meaning that the compounds were extracted reasonably efficiently from the filter. However, additional losses will occur with volatile compounds because of the nature of soxhlet extraction.

Interferences were evaluated in the filters and column and the results are shown in table 2. Lindane, anthracene and PCBs were found in the column, AAQ filter and BQ filters. Obviously, these interferences vary from filter to filter since the AAQ filter was severely contaminated.

Also evaluated was the glass spike carboy used to introduce compounds to the sampler, to observe loss of the analytes at this stage. The most heavily chlorinated compounds, Mirex and PCBs were found in relatively high concentrations in all three washes. Trace amounts of 2,4,5 - trichlorotoluene, lindane and anthracene were also observed in the wash samples.

Table 3 shows the results from the APS testing. No trend was observed in distribution of organic pollutants as a function of turbidity. Those compounds which were found predominately on the filters; octachlorostyrene and mirex; were present even when no particles were added. This would indicate that the compounds are attracted to the glass fiber in the filters.

Interferences were observed in both the columns and the filters although the contamination in the filters was much more severe. It is possible that there were two sources of contamination. The filters showed very high background levels of chlorinated hydrocarbons (PCBs, lindane, anthracene and sometimes 2,4,5 - trichlorotoluene) which would indicate that these compounds are used or produced in the manufacture of the filters. It is uncertain where the interferences from the columns were coming from (a dirty fume hood where samples were prepared is one speculation).

Because of the degree of PCB, lindane and anthracene contamination in the filters and columns it is difficult to observe any distribution pattern. Trichlorobenzene was the only compound found exclusively on the columns. The amount recovered represents approximately 14% of the original amount, which corresponds with the method test recovery value. Trichlorotoluene was found mostly on the column, except when the filters showed contamination of this compound. Mirex and octachlorostyrene were found exclusively on the filters.

TABLE 1

Compound	Percent Recovery		
	Sample Workup Only	AAQ Filter	BQ Filter
1,2,4-trichlorobenzene	14	7	0
2,4,5-trichlorotoluene	81	46	3
Lindane	88	164	96
Anthracene	56	104	20
Octachlorostyrene	35	245	56
Mirex	248	170	71
Benzoperylene	0	0	0
PCBs	121	146	99

TABLE 2

AMOUNT RECOVERED FROM BLANK & WASH SAMPLES

Amount of each compound (ng)

Sample	TCB	TCT	Lin	Ant	Oct	Mir	Ben	PCB
Column Blank	---	---	60	5	---	---	---	202
BQ-Blank #1	---	---	68	10	---	---	---	244
BQ-Blank #2	---	---	227	31	---	---	---	138
AAQ-Blank	---	---	65950	1580400	---	---	---	547
wash #1	---	---	35	8	---	32	---	234
Wash #2	---	16	38	6	---	329	---	269
Wash #3	---	18	60	4	---	316	---	248

TABLE 3

Run#	Filter NTU	Spike	TCF(ng)		TCT(ng)		LIN(ng)		ANT(ng)		OCT(ng)		MIR(ng)		BEN(ng)		PCB	
			C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F
1	0	N	---	---	---	---	187	1548	87	176	---	---	---	---	---	---	150	4513
2	0	Y	63	NA	508	NA	133	NA	696	NA	0.2	NA	59	NA	---	---	217	NA
3	0	Y	29	---	241	80	223	1162	37	319	---	322	---	417	---	---	67	1982
4	0.1	Y	43	---	297	111	352	1265	66	585	---	1006	---	644	---	---	151	1625
5	0.5	Y	27	---	179	78	294	395	53	244	---	303	---	307	---	---	44	606
6	1	Y	43	---	120	21	188	708	40	234	---	220	32	290	78	---	NDM	399
7	5	Y	45	---	203	2767	235	34582	65	464818	---	225	---	217	---	---	221	862
8	10	Y	54	---	321	5695	373	30907	88	590297	---	492	---	265	---	---	604	1426

705

RND detection limit 200 ppb

NA = not available

C = column

F = filter

Spike = 400 ng of each compound was used in each run

TCB = 1,2,4-trichlorobenzene

TCT = 2,4,5-trichlorotoluene

LIN = lindane

ANT = anthracene

OCT = octachlorosytrene

MIR = Mirex

BEN = benzoperylene

PCB = Arochlor 1254 (PBCs)

CONCLUSIONS

Of the eight compounds evaluated in this study, four showed definite distribution behaviour between the columns and the filters. Highly chlorinated, high molecular weight hydrophobic compounds such as Mirex and octachlorostyrene were found exclusively on the filters. Low molecular weight, less chlorinated compounds such as 1,2,4 - trichlorobenzene and 2,4,5 - trichlorotoluene were found almost exclusively on the columns.

The methods used to recover the analytes require improvement. Measures must be taken to more effectively recover volatile compounds such as 1,2,4 - trichlorobenzene and unchlorinated high molecular weight compounds such as benzoperylene. It is also necessary to reduce interferences from the Balston filters. Each filter would require extensive solvent cleaning in a Soxhlet extractor prior to use.

One solution to improve recovery efficiency is to use supercritical fluid extraction (SFE). This method allows selective extraction of a wide variety of compounds from complex matrices. It has the added benefit of reduction in time, labour and the use of toxic solvents. The use of SFE for this application requires additional research.

REFERENCES

1. Ontario Ministry of the Environment and Carleton University, Chemistry department. *Refinement and testing of a preconcentration sampler for dioxins in water*, Final Report, 1989.
2. Ontario Ministry of the Environment, Carleton University and National Health and Welfare. *Large volume sampling methods for analysis of raw and treated drinking water supplies for chlorinated dibenzo-p-dioxins and dibenzofurans, Phase two*. Final report 1987.
3. P.R. Musty and G. Nickless, (1976). J. Chromatogr. 120:369-378
4. J. Lawrence and H.M. Tosine (1976). Environm. Sci. Technol. 10:381-383.
5. G.L. LeBel, D.T. Williams and F.M. Benoit. *Use of Large-Volume Resin Cartridges for the Determination of Organic Contaminants in Drinking Water Derived from the Great Lakes*. Adc. Chem. Ser.214:309-25 (1987).

COMPLETE AMBIENT AIR VOCs AND VOST POHCs ANALYSES USING ONE SINGLE TD/GC/MS SYSTEM

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INTRODUCTION

The determination of ambient air volatile organic compounds (VOCs) and industrial stack principal organic hazardous constituents (POHCs) is a complex task. This is due primarily to: 1. the wide variety of compounds of interest and 2. an ineffective means of analysis. At present, the US EPA suggested a core set of three methods for sampling and analysis of ambient air VOCs (1) and a thermal desorption / purge and trap gas chromatograph / mass spectrometric (TD/PT-GC/MS) identification based procedure for the smoke stack POHC analysis (2). It is worth noting that compounds to be analyzed using these two methods are with similar boiling point ranges. Two sets of equipment are required in order to perform a complete VOC and VOST sample analysis.

In order to maximize the use of existing equipment, we have attempted to evaluate the possibility of using a VOST POHC analytical system to the analysis of ambient air VOCs with boiling point ranges from -30 to 200°C. The same system was used to do analysis on VOST POHCs with boiling point ranges from -30 to 200°C. Presented in this paper are the description of objectives and results obtained

from this work. Preliminary results indicate that complete VOC and POHC analysis was possible on one single system. QA/QC data obtained from the VOST system give good recoveries and standard deviations for VOC compounds with boiling points from 10°C to 150°C.

EXPERIMENT

The VOST TD/PT-GC/MS analytical system consists of a Tekmar LSC2000 thermodesorber (Cincinnati, OH), a Tekmar 4210 autosampler, a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and a Hewlett-Packard 300 series data station. When operated in the VOST POHC analysis mode, a sparger was used to remove excessive water vapor in the VOST sampling cartridge (illustrated in Figure 1). For the ambient air VOC analysis, because relatively low moisture in the VOC sampling cartridge, the sparger was removed to form a thermal desorption / gas chromatograph / mass spectrometer system (TD/GC/MS).

An adsorbent analytical trap was used to concentrate both VOCs and POHCs for the subsequent GC/MS analysis. In the POHC analysis, the TD/PT-GC/MS used a standard Supelco adsorbent trap (Supelco Cata. # 2-0321, Oakville, Ontario). In the VOC analysis, a proprietary trap (3) was used in the TD/GC/MS system. Spiking mixtures were prepared using a modified gas mixing chamber (La-sale Glass, Barrie, Ontario). All data presented was obtained from both within run and between run experiments.

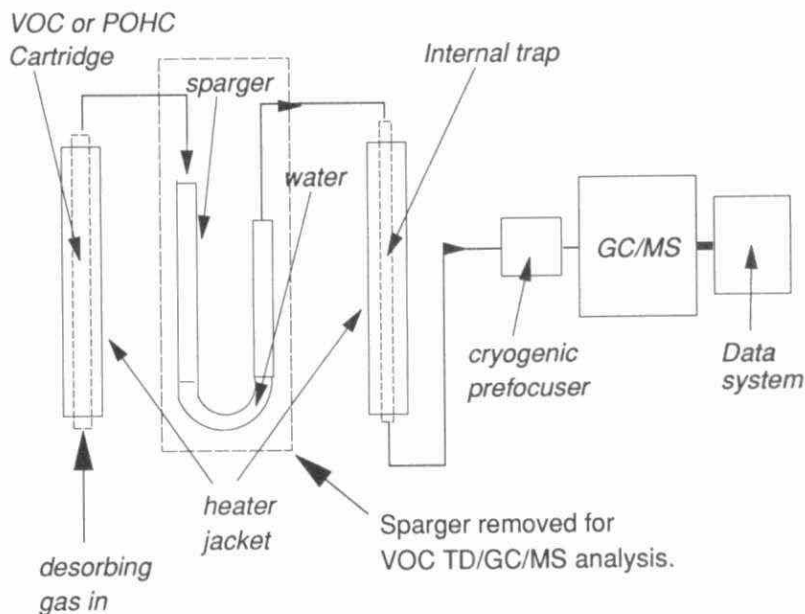


Figure 1. Block diagram of TD/PT-GC/MS and TD/GC/MS for VOST POHC and ambient air VOC analysis, respectively.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the total ion chromatogram (TIC) obtained from the VOST TD/PT-GC/MS system. Figure 3 illustrates the TIC when operating this same system in the TD/GC/MS mode for the VOC analysis. Table 1 illustrates the evaluating results of the 26 VOST POHCs of the Ontario Ministry of the Environment (MOE). It is worth noting that both the low and the high boilers have much

worse standard deviations than the compounds with boiling points from 10°C to 150°C. Each set of standard deviation data represents nine consecutive within run analysis of the 26 VOST POHCs. The analysis time, starting from the thermal desorption to the complete data analysis, was about 3 hours/sample. There was a time gap of 8 days between the collection of these two set of data.

Table 2 lists the evaluating results of 12 of the 36 VOCs in the MOE method (4). These 11 compounds were selected to represent a boiling point range from -32°C to 225°C. Again, one could obtain similar results to that from the 26 VOST POHCs.

CONCLUSION

We have demonstrated the ability of applying one single system to the analysis of both VOST POHCs and ambient air VOCs. Possibility of eliminate a cryogenic trap for the TD/GC/MS analysis offers a cost effective approach for the VOC analysis. Time required to convert a TD/PT-GC/MS to a TD/GC/MS, or vice versa, is about 30 minutes. One could dynamically allocate existing systems to smooth unexpected workload. Problems related to instrument downtime would have been alleviated, achieving a constant, maximized sample throughput.

REFERENCES

1. "Compendium of methods for the determination of toxic organic compounds in ambient air", R.M.Riggin, Battelle-Columbus Laboratories, Columbus, Ohio.
2. "Protocol for the collection and analysis of volatile POHCs using VOST", E.M. Hasen, Envirodyne Engineers, St. Louis, Missouri.
3. Robert Belardi, Supelco Canada, Oakville, Ontario, private communication.
4. "The determination of volatile organic compounds in ambient air by thermal desorption", Ontario Ministry of the Environment Method PATH123-E3131a.1, Rexdale, Ontario.

TABLE 1. QA/QC DATA OBTAINED FROM TD/PT-GC/MS SYSTEM FOR THE VOST[®] POHC ANALYSIS.

COMPOUNDS (B.P., °C)	AMOUNT	STANDARD DEV. [*]	
	SPIKED (ng)	FIRST	SECOND
DICHLORODIFLUOROMETHANE (-29.8)	617.8	47.12	132.76
VINYLCHLORIDE (-13.9)	319.5	29.71	41.97
BROMOMETHANE (4.0)	485.4	N/A	N/A
TRICHLOROFLUOROMETHANE (24.0)	277.6	12.92	10.50
ACETONE (56.5)	118.7	163.27	67.06
1,1-DICHLOROETHENE (31.9)	182.7	2.33	6.74
TRICHLOROTRIFLUOROETHANE (46.0)	236.8	N/A	5.65
METHYLENE CHLORIDE (39.8)	198.8	22.12	23.16
TRANS-1,2-DICHLOROETHANE (48.0)	189.0	5.15	8.07
CHLOROFORM (61.0)	222.6	6.41	6.94
1,1,1-TRICHLOROETHANE (74.0)	200.6	9.94	10.88
1,2-DICHLOROETHANE (84.0)	188.4	4.10	5.16
BENZENE (80.1)	131.8	4.30	7.67
1,2-DICHLOROPROPANE (96.8)	174.0	4.38	7.98
TRICHLOROETHENE (86.8)	219.0	3.48	3.94
BROMODICHLOROMETHANE (90)	295.7	5.33	6.49
TOLUENE (110)	129.9	5.87	7.29
DIBROMOCHLOROMETHANE (119)	357.0	4.56	5.49
ETHYLENE DIBROMIDE (131)	405.2	5.64	6.69
TETRACHLOROETHENE (121)	243.5	3.54	5.14
ETHYLBENZENE (136)	129.9	5.79	8.00
M/P-XYLENE (138)	129.5	6.30	10.90
BROMOFORM (149.5)	433.5	4.05	41.61
O-XYLENE (144)	132.0	6.29	10.51
CUMENE (169)	129.3	5.45	7.82
MESITYLENE (164)	129.6	41.54	14.32

* Presented in $\pm\%$ to the spiked amount. There was an 8-day time gap between the first and the second set of data. Both sets of data were obtained from 9 within-run experiments.

TABLE 2. QA/QC DATA OBTAINED FROM TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*
METHYL CHLORIDE (-23)	103.3	21.4
VINYL CHLORIDE (-13.9)	136.8	16.22
1,3-BUTADIENE (-4.5)	97.5	17.41
1,1-DICHLOROETHANE (31.9)	182.7	19.02
TRICHLOROMETHANE (61)	222.6	29.3
BENZENE (80)	131.8	33.03
BROMODICHLOROMETHANE (90)	295.65	31.07
TOLUENE (110)	129.9	23.62
1,2-DIBROMOMETHANE (131)	405.11	30.48
CHLOROBENZENE (131)	166.11	21.05
1,2-DICHLOROBENZENE (180)	195.0	9.48
NAPTHALENE (217)	174.3	16.61

* Presented in $\pm\%$ to the spiked amount. The data was obtained from 11 within- run experiments.

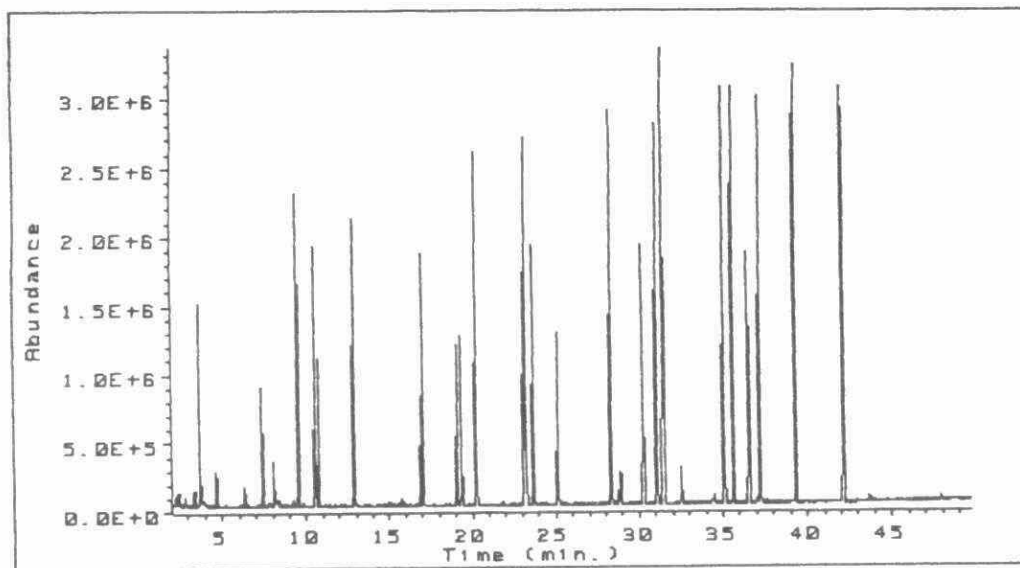


Figure 2: Total Ion Chromatogram obtained from the VOST TD/PT-GC/MS system.

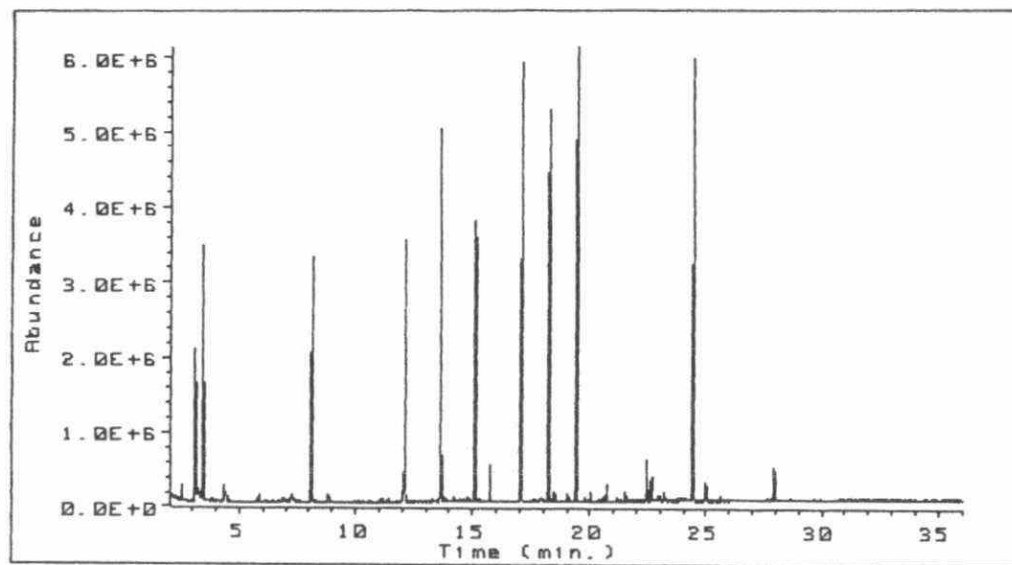


Figure 3: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system.

AN AUTOMATED GEL PERMEATION CHROMATOGRAPHIC METHOD FOR CLEANUP OF SEWAGE SLUDGE EXTRACTS FOR GC/MS ANALYSIS OF PRIORITY ORGANIC POLLUTANTS

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The increasing emphasis placed on water pollution and hazardous waste control, backed by stringent regulations such as Ontario's Municipal and Industrial Strategy for Abatement (MISA) program has increased the interest in the behaviour and fate of a wide range of organic contaminants during the wastewater treatment process. One result of this process is the annual production of approximately 7 million cubic meters of sludge. Treated sludges find many uses (1) including:

- co-disposal in landfill sites;
- agricultural land or land stabilization application;
- used as a fuel for low temperature incineration/power production;
- anaerobic digestion/evolution of methane gas;
- added to animal feeds (after suitable prescreening for contaminant levels).

Given these potential uses and the fact that many organic chemicals which enter wastewater treatment systems are ultimately retained in the sludge it is important to establish the nature and concentrations of these pollutants.

To satisfy the needs of investigative and regulatory environmental monitoring, the TO section of the LSB has been developing a rapid GC/MS method for the analysis of sewage sludges. Organic compounds investigated include:

- 40 base neutrals;
- 20 phenolics;
- 7 phenoxy acid herbicides;
- polychlorinated Biphenyls;
- 30 chlorinated hydrocarbons (pesticides and industrials).

These target organic compounds may be present in sludges (2) either in: solution, colloidal suspension, or absorbed on particulate matter.

This coupled with the chemical complexity of sludge, including high and variable organics and solids content, present major problems in the determination of trace levels of organic priority pollutants.

The objective of this research project was to develop an effective, and rapid analysis procedure which would quantitatively extract the target components, and consistently separate them from the co-extracted interferences including lipids, fatty acids, hydrocarbons and other high molecular weight compounds (3). Gel Permeation Chromatography (GPC) is a widely used technique in biochemical analysis and a large number of papers had been published [4-11] describing the cleanup of environmental sample extracts such as fish, sludge, solid waste, soil and sediments. In this regard the application of Gel Permeation Chromatography (GPC) was evaluated and an automated rapid cleanup procedure was devised.

Experimental

Apparatus - Shimadzu High Performance Liquid Chromatograph equipped with a SIL-6B Autoinjection (modified with a 2 ml injection loop) and Advantec SF-2120 Superfraction collector. Column - 600mm x 30mm packed with 60g of Bio-Beads SX3 (Bio-Rad Laboratories).

Elution Solvent - Methylene chloride-cyclohexane (1:1,V/V) flow rate 2 ml/min.

Calibration mixture - A standard mixture was prepared by dissolving Di-n-octylphthalate, Benzyl butyl phthalate, Methoxychlor and 4-nitrophenol in Methylene chloride (5 μ g/mL) of each compound).

Sample Preparation

Sewage sludge(s) varying in consistency from 0-20% solids was homogenized and a 25g portion was extracted with a mixture of solvents (Diethylether/methylene chloride 2:1, V/V). The extract was concentrated to 2 ml. A 0.5 ml extract was injected in the GPC system for cleanup.

Results and Discussion

- In our preliminary studies, two conventional open column chromatography cleanup approaches were evaluated using a Gel Permeation Chromatography (Bio-Beads SX) and polarity separation (Florisil).
- Qualitative GC/FID screening of the extracts cleaned on Bio Beads SX (collecting one fraction) do not appear much different from those of extracts cleaned up by Florisil Column Chromatography. Both of these extracts proved to be too complex (i.e. too much interfering material) to analyse by GC/MS.
- The cleanup on Bio-Beads SX was repeated employing an HPLC system.
- The packings and solvent system evaluated were:
 - Bio-Beads SX2 - Methylene Chloride
 - Bio-Beads SX3 - Methylene chloride/cyclohexane (1:1,V/V)
 - Bio-Beads SX8 - Methylene chloride/cyclohexane (1:1,V/V)
- Bio-Beads SX3 - gave the best results and was selected for further work.

Collecting all our target compounds in one fraction gave unsatisfactory results, so a fractionation procedure was developed. In order to calibrate the system and determine the optimum fractionation window size, the standard mixture was separated on the Gel Permeation Chromatography system.

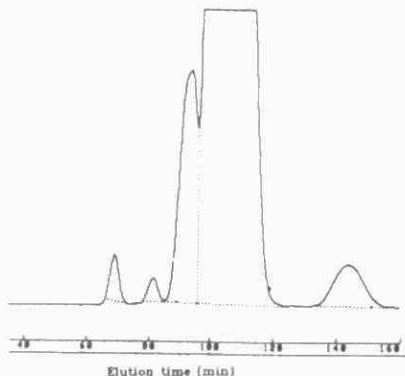
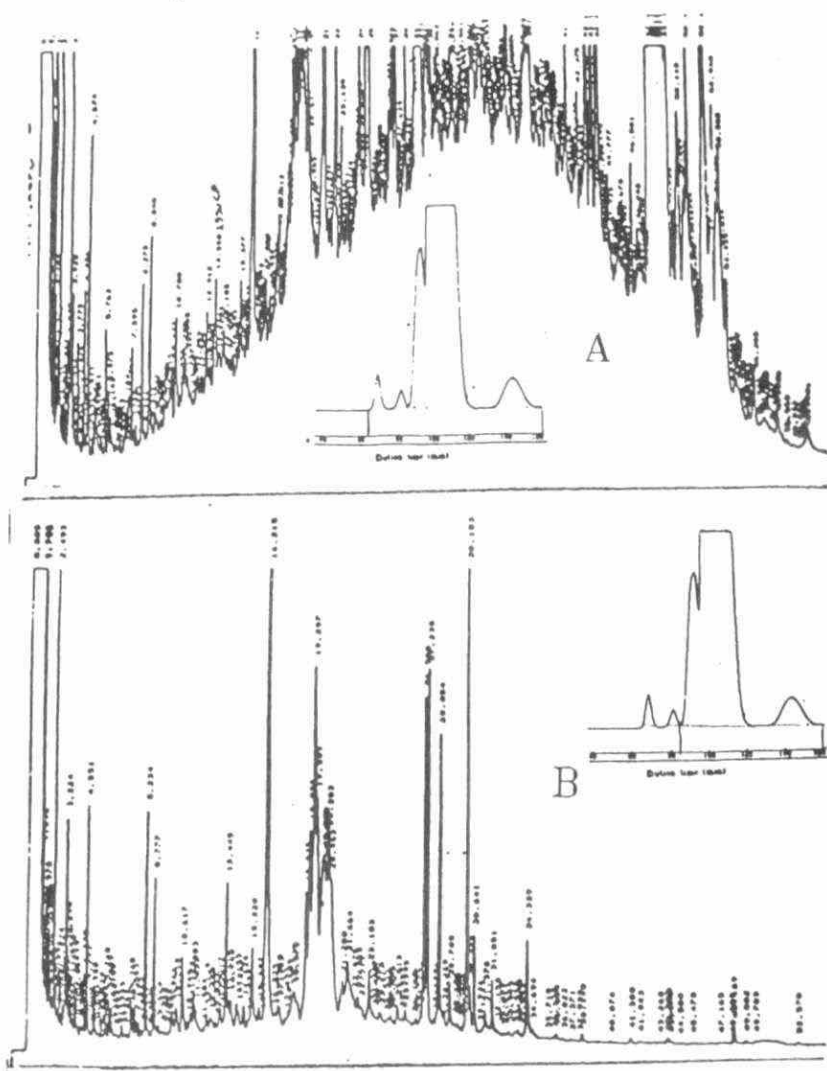


Fig. 1 - GPC elution profile of a standard mixture eluted with CH₂CL₂/CYCLOHEXANE (1:1) on Bio-Beads SX-3(60g)



Two fractions were collected.

Fraction I from 62 min (when the first compound Di-n-octylphthalate elutes) to 82 min (at the valley between benzyl butyl phthalate and the Methoxychlor).

Fraction II collected from 82 min (when Methoxychlor elutes) to 157 min (after our last eluting compound 4-nitrophenol).

Fraction I contains all phthalates as well as the majority of interferences.

Fraction II contains all of the target compounds.

To illustrate the advantage of GPC fractionation procedure, see Fig. 2.

Summary and Conclusions

- This work is part of the effort to develop an analytical method for the determination of a wide range of organic contaminants in STP sludges.
- A number of GPC packing (Bio-Beads) for the cleanup of sludge extracts were investigated, ranging from SX3 to SX8.
- Bio-Beads SX3 were confirmed as the resin of choice for this type of work, in agreement with other researchers.

Sacrificial separation of a first fraction containing mainly phthalates virtually eliminated interferences from second fraction containing all other target priority pollutants.

- Separation conditions were optimized and then automated to provide an extract suitable for direct GC/MS analysis.
- The sacrificed fraction can be utilised for the analysis of phthalates after further cleanup on Florisil.

Literature cited

- (1) Paul Cheremisinoff, Pollution Engineering Dec. 1988 p. 66-73.
- (2) H.R. Rogers, and all, Nat. Res. Vol. 23, No. 7, pp 913-921 1989.
- (3) V. Lopez Avila and all
Advances in the Identification and Analysis of Organic Pollutants in water Vol. 2 Chapter 43, L.H. Keith, Ed. (Ann Arbor, MI: Ann Arbor Science Publisher Inc, 1976).
- (4) Analytical Methods for the National Sewage Sludge Survey, US EPA method 1618.
- (5) US EPA - 600/2-80-196 GC/MS Methodology for priority organics in municipal wastewater treatment - F. Bishop.
- (6) US EPA - 600/2-80-020 - Method development for determination of polychlorinated hydrocarbons in municipal sludge - Charles F. Rodrigues and all.
- (7) US EPA - Aug. 1988 Analytical Methods for the National Sewage Sludge Survey.
- (8) C.J. Musial and Y.F. Uthe. J. Assoc. Off. Anal. Chem. (Vol. 69, No. 3, 1986).
- (9) D.L. Stalling, R.C. Tindle, and J.L. Johnson - Journal of the AOAC (Vol. 55, No. 1, 1972)
- (10) Burns et all J. Assoc. Off. Anal. Chem. (Vol. 64, No. 2, 1981).
- (11) J.M. Czuczwa and A. Alford - Stevens - J. Assoc. Off. Anal. Chem (Vol. 72, No. 5 1989).

SIMULTANEOUS DERIVATIZATION - EXTRACTION TECHNIQUE FOR THE ANALYSIS OF ACIDIC ORGANIC CONTAMINANTS FROM WATER - FEASIBILITY STUDY WITH DIAZOMETHANE FOR THE ANALYSIS OF 4-AMINO - 3,5,6-TRICHLOROPICOLINIC ACID (PICLORAM)

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Picloram (4 amino-3,5,6-trichloropicolinic acid, is a herbicide widely used, for the control of woody and broad leaf plants in pastures, small grains, timberland and various rights of way.

Even though Picloram is highly active at low application rates, is relatively non-toxic to animal species; its wide-spread usage and resistance to degradation raises concerns regarding environmental levels and fate. Various procedures have been developed to determine residues of Picloram in soil, plants, sediments and water. Techniques such as High Performance Liquid Chromatography (HPLC) suitable for the analysis of commercial formulation without derivatization as well as Gas Chromatographic methods which typically determine Picloram as the methyl ester, 2-chloroethyl ester or pentafluorobenzyl derivative. For multicomponent environmental analysis, solvent extraction followed by derivatization and gas chromatographic analysis is the most common technique. However, the performance of these methods, especially in the area of multicomponent environmental applications can be highly erratic and biased low. Recoveries reported by various authors vary from 97(1) to 59(2) percent and it is not uncommon to find values lower than these.

This paper describes the development of a rapid, simultaneous extraction - derivatization procedure (3) for the analysis of picloram in water which provides consistent (>86%) recoveries. The research finding also provides an insight into the possible source of analytical variability related to the chemical properties and equilibrium of Picloram in aqueous solution.

Experimental

Apparatus - Gas Chromatograph Hewlett Packard 5730 with dual Ni63 electron capture detectors. The instrument is fitted with one split/splitless capillary injector system, HP7672A autosampler, HP33804 dual pen strip chart recorder, all interfaced with the HP1000 computer system.

Columns - capillary columns 30m x 0.25mm D1701 and DB1.
Temperature program: initial 90 C, hold 2 minutes programming rate 4 C/min, hold at 270 C for 8 minutes. Injector temperature 250 C, Detector temperatures 300 C.

Procedure - unless otherwise stated all experiments were carried out under the following conditions:

- The water spiked or containing the target analytes sample (800 ml) was acidified (HCl) to pH1.
- Dichloromethane (30 ml) was added and mixed well.
- Diethylether (60 ml) was added and mixed well.
- The two layers were allowed to separate and diazomethane (DAM) solution 1 ml (prepared from 21,5g of N,N-Dimethyl N,N-Dinitrosoterephthalamide made up to 37 ml with diethyl ether) was added with a pipette to the top solvent layer in a circular motion.
- The reaction mixture was allowed to stand for 10 minutes.
- The mixture was shaken well and diazomethane addition was repeated twice.
- The mixture was allowed to stand for 2 hours.

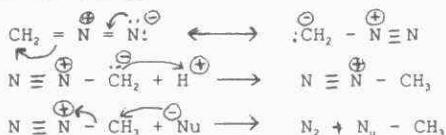
After this, the organic layer was separated and concentrated on a rotary evaporator (addition of more methylene chloride will sink the solvent to form a bottom layer if this is more convenient to separate).

Results and Discussion

Chemical Consideration

Superficial examination of the chemical structure of Picloram, a carboxylic acid with two different amino functions, would make one conclude that it has amphoteric properties. In practice, Picloram behaves as a fairly strong organic carboxylic acid and significant protonation of the amino functions does not occur above pH 0.8. This can be explained by the strong combined electron withdrawing effects of the chlorine and carboxyl substituents (4). The aqueous solubility of Picloram is strongly pH dependent. Even in the narrow range of pH 0.84 to pH 2.68 the solubility increases seven fold from 63 mg/L to 445 mg/L (5). During extraction with an organic solvent it is the undissociated form of Picloram that is extracted. Since both the concentration of undissociated picloram and its aqueous solubility are highly pH dependent, the partition coefficient will also vary with the pH. This may be one of the reasons for erratic recoveries. If Picloram could be derivatized during the extraction step, the formation of a neutral species would shift the complex, simultaneous equilibria in favour of the extraction.

The use of diazomethane was explored during the extraction step to convert Picloram to its methyl ester. It is expected that diazomethane will have a very short lifetime in strong acidic aqueous media because the formation of the protonated reagent is promoted and the latter can react with most nucleophile (Nu^\ominus) including water



The presence of extraction solvent in the aqueous reaction mixture will protect diazomethane from rapid decomposition and permit the target reaction to proceed with less competition from non target nucleophiles.

Even if little methyl ester formation takes place in the aqueous phase, portion wise addition of diazomethane to the solvent layer will esterify the already extracted Picloram and extraction of a further quantity of Picloram can begin once again without removing the solvent.

Thus while minimizing the effects of pH on the process, addition of 2-3 portions of diazomethane solution (followed by thorough mixing) becomes practically equivalent with extraction by 2-3 aliquots or organic solvent see Table 1 and 2.

Table 1

RECOVERY OF PICLORAM (SPIKING LEVEL 1ppb) USING DIFFERENT ACIDS AND SIMULTANEOUS DERIVATIZATION/EXTRACTION PROCEDURE.

Acid used at pH (1-2)	% Recovery
H ₃ PO ₄	102
HCL04	110
HC004	40
H ₂ S04	98,89
HCl	97,106,83*

*Diazomethane added in 1 portion

Recoveries of seven acid herbicides from fortified 800 ml water samples are presented in Table 2.

The recoveries of all seven herbicides were good and ranged from 77 to 111%.

Recovery reproducibility proved excellent.

Table 2

RECOVERIES (%) OF ACID HERBICIDES FROM FORTIFIED (APPROX. 1 μ g/L LEVEL) 800 mL WATER SAMPLES BY SIMULTANEOUS EXTRACTION DERIVATIZATION PROCEDURE

HERBICIDE #1	DAM three portions								SD	DAM one portion	
	#2	#3	#4	#5	#6	#7	AVG			#1	#2
DICAMBA 95	88	90	99		93	97	94	4		87	97
24DP 99	95	98	102	77	97	98	95	8		101	99
24D 111	104	110	113	95	112	111	108	6		116	111
SILVEX 105	100	101	104	86	95	100	99	6		108	95
245T 107	104	105	107	100	101	102	104	3		112	106
24DB 108	104	105	107	104	103	103	105	2		114	107
PICLORAM 101	105	106	100	100	97	97	101	3		86	77

The results in Table 2 show the application of the simultaneous extraction-derivatization procedure to acidic compounds in the full scan including Picloram. The generally excellent recoveries indicated a wide applicability for this technique. Further study is underway for the use of this simple and effective method for other groups of acidic compounds, such as resin and fatty acids. Preliminary results are most encouraging.

- (1) Allan Y. Cessna, Ray Grover, Lorne A. Kerr, and Melonee L. Aldered, *J. Agric. Food Chem.* 1985,33,504-507.
- (2) Hing-Biu Lee, Yvonne D. Stokker and Alfred S.Y. Chau, *J. Assoc. Off. Anal. Chem.* Vol. 69, No. 3, 1986.
- (3) E.J. Eisenbraun, R.N. Morris and G. Adolphsen, *Journal of Chemical Education* 47, 710(1970).
- (4) Max W. Cheung and James W. Biggar, *J. Agr. Food. Chem.*, Vol. 22, No. 2, 1974.
- (5) J. Osteryoung and Jeffrey W. Whittaker, *J. Agric. Food Chem.* 1980,28,95-97.

Brominated and Mixed Bromo/Chloro
Dibenzo-p-dioxins and Dibenzofurans:
Toxicological Properties, Analytical
Methods and Occurrence

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INTRODUCTION

Considerable information has accumulated over the past two decades regarding the synthesis, analytical methodology, environmental distribution and biological activity of polychlorinated dibenzo-p-dioxins (CDDs) and dibenzofurans (CDFs). CDDs and CDFs are known to exist as trace contaminants within certain commercial products prepared from chlorinated phenols (and their phenoxy acid derivatives), polychlorinated biphenyls (PCBs), and other chlorinated aromatic compounds. In addition to these chemical sources, CDDs and CDFs are also derived from burning and other high temperature processes and are considered to be associated with combustion whenever organic materials and a suitable source of chlorine are present.

In contrast, very little has been reported concerning the potential environmental importance of polybrominated dibenzo-p-dioxins (BDDs), dibenzofurans (BDFs) and mixed bromo/chloro dibenzo-p-dioxins and dibenzofurans (CBDDs and CBDFs). These classes of compounds are of interest owing to their structural similarities to the CDDs and CDFs. Furthermore, BDDs and BDFs are also found as impurities in commercial products (eg. brominated flame retardants) and both BDDs/BDFs and CBDDs/CBDFs have been observed as thermal reaction products from the appropriate precursors. Lastly, these classes of compounds are expected to exhibit biological activity similar to their chlorinated analogues and

hence their presence in the environment is a cause for concern.

TOXICOLOGICAL/BIOLOGICAL EFFECTS

There is very little information in regards to the toxicity of these compounds, however the data that is available indicates that some of the congeners do pose a potentially significant health hazard. For example, in guinea pigs 2,3,7,8-tetrabromodibenzofuran has been found to be as potent as its chloro analogue (2378-TCDF) and their toxic symptoms are similar. In the rat 2,3-dibromo-7,8-dichlorodibenzo-p-dioxin is more toxic than 2,3,7,8-TCDD and 2,3,7,8-TBDD is equipotent with 2,3,7,8-TCDD.

SOURCES/OCCURENCE

BDDs and BDFs have been detected in many of the brominated flame retardants and also in their pyrolysates. Moreover, when brominated flame retardants are mixed with chlorine containing plastics (eg. PVC) and pyrolyzed CBDDs and CBDFs are formed.

Recently, as expected, these compounds (BDDs, BDFs, CBDDs, CBDFs) have also been found in ash samples from an MSW incinerator although the levels are much lower than the CDD and CDF levels.

ANALYTICAL PROCEDURES

From the available literature, it would appear that the methods commonly used for CDD/CDF analysis can be used for the analysis of the bromo and mixed bromo/chloro analogues. GC/MS would appear to be the instrument of choice for final detection and quantitation.

Capillary GC would be preferred due to the number of theoretically possible congeners involved; there are 1550 CBDDs and 3050 CBDFs possible. Also, due to the molecular weights of some of the congeners high resolution MS would be more suitable than quadrupole MS.

Currently, there are standards, including C13-labelled surrogates, available from two sources. These compounds are very difficult to prepare in good quantities and are also somewhat unstable.

DETERMINATION OF ORGANOLEAD COMPOUNDS IN INDUSTRIAL EFFLUENTS

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SUMMARY

Organolead compounds are used as "anti-knocking" agents in gasoline to increase the efficiency and longevity of high compression engines. The toxic affect of these compounds on humans is well known. Governments in North America have now restricted the use of these compounds in gasoline, however many other parts of the world such as Europe and Asia have not. In Ontario, these compounds are produced for export overseas.

The Ontario Ministry of The Environment has set guidelines for the amounts of organolead compounds in industrial effluents. The Ministry has developed a method for analyzing these compounds for regulation monitoring. This paper describes the development of this method, instrumental optimization, in-situ derivitization/extraction and quality control data.

INTRODUCTION

Despite the benefits of organolead as an octane enhancer and a valve seat lubricant, scientific research has demonstrated conclusively that negative health and detrimental environmental effects of lead far outweigh it's advantages as a gasoline additive. Acute lead poisoning has been reduced in North America because of the use of "unleaded gasolines". However, chronic exposure to low levels of lead in the environment still remains a serious concern. In the mid 1980's, governments in North America restricted the use of lead in gasoline. Farm and aviation fuel are the only known exceptions. Although organolead compounds are not being used locally in gasoline, they are still being produced for export overseas in Ontario. The municipal and industrial strategy for abatement (MISA) program incorporated by the Ontario Ministry of the Environment dictates that it is the responsibility of the industry or municipality to monitor and control, to provincial guidelines, the concentration of pollutants in their effluent. Regulation monitoring is conducted by the Ministry on a random basis to assure the company is conforming to the provincial guidelines. For this purpose, the Laboratory Services Branch has developed a method for analyzing organolead compounds in industrial effluent.

Methods available for the determination of alkyl lead compounds include spectrophotometric measurements of their dithizonates in chloroform at different wavelengths¹, and of their dialkyllead complexes with 4-(2-pyridylazo)resorcinol after conversion of the trialkyl lead to dialkyllead with iodine monochloride². These methods are lengthy and lack speciation.

Other methods include gas chromatography (GC) with an electron capture detector³, gas chromatography - microwave induced plasma - atomic emission detection (GC-MIP-AED)⁴, and gas chromatography - atomic absorption spectrophotometry (GC-AAS)⁵. All of these methods use an extraction of lead compounds from an aqueous solution after chelation with appropriate reagents.

The combination of gas chromatography and atomic absorption spectrophotometry has proved to be an excellent technique for the determination of the above compounds because of its sensitivity and the ability to speciate and will be used for this method. The compounds to be analyzed are tetramethyl (Me_4Pb), tetraethyl (Et_4Pb), trimethyl (Me_3Pb), triethyl (Et_3Pb), dimethyl (Me_2Pb) and diethyl (Et_2Pb) lead.

EXPERIMENTAL

A Hewlett Packard 5890 Gas Chromatograph (GC) equipped with a Supelco megabore fused silica DB1 capillary column (30 m in length X 0.530 mm I.D. - 1.4 μm film thickness) was used for separation. The transfer line was constructed of 1/16" I.D. stainless steel tubing about 3 ft in length. The quantitation was performed by using a Perkin-Elmer 2380 atomic absorption spectrophotometer (A.A.) with a quartz furnace for atomization. The data was recorded on a Varian 7240 integrator.

The operating conditions for the GC were set at 150 degrees celsius for the injection port temperature and 0 - 200 degrees celsius for the oven temperature at programmed stages. The transfer line was heated to 70 degrees celsius with nitrogen carrier gas flowing through at 10 ml/min. The A.A. wavelength was set at 217.4 nm with a slit width of 0.7 nm. The quartz furnace was heated to 900 degrees celsius.

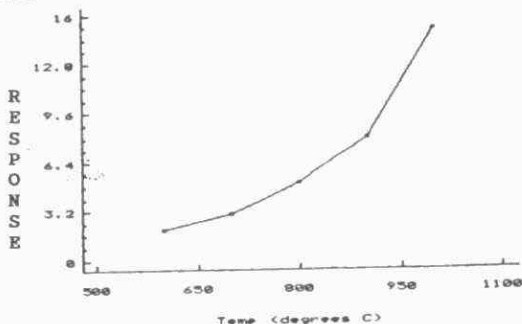
Sample Storage and Preparation

The samples were received in 1 litre amber glass bottles lined with teflon caps. They were stored at 4 degrees celsius and the analysis was performed within 2 weeks. The sample preparation involved removing a 10 - 11 ml sample and displacing it with 10.0 ml of hexane. The bottle was capped and rotary tumbled for 30 min. The organic phase was separated, dried with anhydrous sodium sulphate and analyzed. The volume of the remaining sample was adjusted to 800 ml. Sodium chloride (50 g) and aqueous 0.5M sodium diethyldithiocarbamate (50 ml) were added to the sample. The solution was extracted with 2 X 50 ml hexane. It was rotary tumbled for 30 min with each extraction. The organic phase was separated and dried with sodium sulphate. Toluene (4 ml) was added to the extract and then it was concentrated to 3 - 4 mls. Butyl Grignard reagent (Aldrich, 1.9M in THF) at a volume of 0.5 ml was added, mixed and kept at room temperature for 10 min. The volume was adjusted to 5.0 ml with toluene. It was then cooled in an ice bath and washed with 4-5 ml of 0.5M sulphuric acid to destroy the excess Grignard reagent. A portion of the extract was dried with sodium sulphate and analyzed for trialkyl and dialkyl lead compounds.

RESULTS AND DISCUSSION

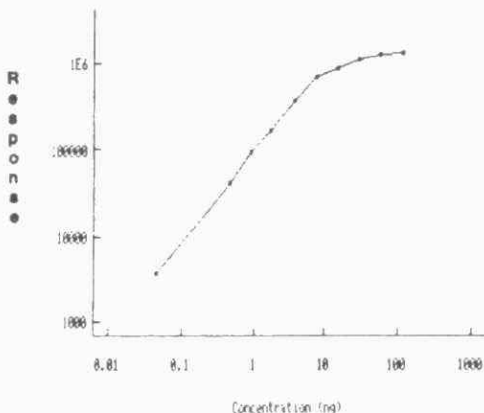
1. Instrument Optimization. The optimization of the instrumentation included injection port temperature, carrier gas flowrate, oven temperature, A.A. slit width, A.A. wavelength, furnace temperature, furnace alignment, hydrogen flowrate and transfer line temperature. The most critical parameter was furnace temperature. An optimum was not reached due to the thermal breakdown of the furnace winding. Consequently, optimum sensitivity is not achieved. More experimentation with a heavier gauge furnace wire will be conducted in the future. A compromise temperature of 900 degrees celsius was used. A response profile for several furnace temperatures is shown in FIG 1.

FIG 1. Profile - Response VS Furnace Temperature
50 ppb Tetraethyl Lead



2. Linear Dynamic Range. The linear dynamic range was determined to be approximately 3 orders of magnitude from the instrument detection limit. FIG 2. shows a response while varying concentrations of tetraethyl lead.

FIG 2. Concentration VS Response - 50 ppb Tetraethyl Lead



3. Quality Control Data.

Recovery studies were performed by spiking double distilled water samples at 20 and 50 ug/l. Eight replicates were spiked and analyzed and the data is given in Table 1 and Table 2. The method detection limits (MDL'S) were determined to be 0.5 to 2.0 ug/l and were calculated according to method development protocol⁶. The quality control data on dialkyl lead compounds was not available because of the lack of pure standards. Future attempts to synthesize purer standards will be conducted.

Table 1. Recovery Data @ 20 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me ₄ Pb	87 - 96	11	0.8
Et ₄ Pb	80 - 112	21	2.0
Me ₃ Pb	90 - 104	2	0.5
Et ₃ Pb	85 - 110	9	1.0

Table 2. Recovery Data @ 50 ug/l. n = 8 replicates

Parameter	Recovery(%)	%RSD	MDL(ug/l)
Me ₄ Pb	93 - 96	5	0.5
Et ₄ Pb	90 - 106	10	2.0
Me ₃ Pb	90 - 114	10	1.5
Et ₃ Pb	85 - 110	8	1.0

The method was successfully tested on an actual industrial effluent. The data obtained by standard addition in six industrial effluents was found to be within the limits reported in Table 1 and Table 2.

CONCLUSIONS

1. The instrumental optimization was performed. The furnace temperature of the A.A. was found to be the most critical parameter on sensitivity.
2. A method has been established for the analysis of tetra alkyl and tri alkyl lead compounds. Detection limits, linear dynamic range, precision and extraction efficiency data were within the MISA methods development protocol.
3. Work for the determination of di alkyl lead compounds is in progress.

REFERENCES.

1. S.R. Henderson and L.J. Synder, *Oxal Chem*, 33 (1961) 1172.
2. F.G. Noden, in M. Brianca and Z. Konrad (Eds.), *Lead in the Marine Environment*, Permagon press, Oxford, 1980, p 83 ff.
3. K. Hayakawa, *Jap. Hyg.*, 26 (1971) 377.
4. S.A. Estes, P.C. Uden and R.M. Barnes, *Anal Chem.*, 53 (1981) 1336.
5. Y.K. Chau, P.T.S. Wong and O. Kramer, *Analytica Chimica Acta.*, 146 (1983) 211-217.
6. *Estimation of Analytical Method Detection Limits MDL - MISA - document - ISBN 0-7729-4117-3*).

TECHNIQUES FOR THE IDENTIFICATION OF SPECIFIC SOURCES OF AIRBORNE PARTICULATES

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Introduction

Source identification for airborne particulates is important both to insure effective remedial action and to assess potential health risks associated with specific air masses. Three methods for source identification are especially promising: elemental isotope distribution, trace element distribution and surface reactivity of the particles. A wide variety of experimental techniques are available at The University of Western Ontario including Secondary Ion Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) and Ion Chromatography (IC). Other techniques are available such as Neutron Activation Analysis (NAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). We have confined our initial studies to the instruments readily available at The University of Western Ontario or at the Ontario Ministry of the Environment Laboratories. In addition we have sought to focus attention, where possible, on instrumentation which can be used in simple tests with a relatively unskilled operator. The main thrust of the report will be to examine the results obtained by IC and SIMS, the former is by far the easier technique. Some ICP-MS will also be reported

We have established that XPS and SEM were of limited utility without detailed study. XPS results are limited because the technique is surface sensitive (i.e. to two or three monolayers), the samples are prone to charging and are widely distributed on the filter surface. SEM has high detection limits ($\sim 1\%$) and with current instrumentation is not capable of detecting carbon, an element of special interest because it is abundant in atmospheric particles originating from combustion. FTIR showed the principle species in assemblies of particulate matter to be NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, though organic functional groups such as carboxylates could be identified. The area will be pursued more vigorously in the future. NAA studies are underway but the technique is expensive, time consuming and produces low-level nuclear waste.

Finally early SIMS measurements show that there is insufficient material in a normal air sample to carry out isotopic analysis of the surface material. Accordingly we have chosen to study elemental distributions using SIMS imaging techniques. In addition we have chosen to assess the surface reactivity of air particulate material by measuring catalytic activity on the reaction: $\text{SO}_3^- \longrightarrow \text{SO}_4^-$.

This reaction was chosen because it has interesting environmental consequences (acid rain), may be indicator of the potential health effects of atmospheric particles and is easily followed using IC.

Experimental

1. Sample Collection

Sample were collected on glass fibre filters using high volume samples, by the Ontario Ministry of the Environment.

2. Trace Metal Analysis

Trace metal concentrations were obtained using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. For each filter, two samples were made. The samples were prepared to determine the total metal concentration and the concentration at pH 5. The samples prepared for total metal determination was made by leaching a filter in 3% nitric acid for 30 minutes and filtration through a 0.8 μm Nucleopore filter. The samples prepared for metal determination at pH 5 were made by leaching the filter at pH 5 for 30 minutes and subsequent filtration through a 0.8 μm Nucleopore filter with stabilization in 0.5% nitric acid (100 μl of 35% nitric acid in 7 ml sample).

3. Ion Chromatography and the $\text{SO}_3^{2-} \longrightarrow \text{SO}_4^{2-}$ Reaction

The oxidation of S(IV) is pH dependent with the exact reactive species depending on the nature of the equilibrium system¹⁻⁶. However, it is generally agreed that the oxidation of S(IV) to S(VI) decreases as the aqueous phase becomes acidic⁷. Since the reaction is highly pH dependent, a buffer was used to control the pH. The buffer chosen was a 10 mM $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3\text{CO}_2\text{H}$ buffer at pH 4.7, standardizing all the S(IV) oxidation tests.

The S(IV) oxidation test consisted of analyzing two planchets from one filter. Assuming the distribution of material on the filter was homogeneous, one piece of filter was used as the blank to determine the initial concentrations (or loadings) of the anions present (Cl^- , NO_3^- , SO_3^{2-} and SO_4^{2-}) on the filter and the other was used to test the S(IV) oxidation reactivity in a buffered solution. The blank sample was prepared by immersing the filter in 10.00 ml of distilled-deionized water (DDW). The second piece was immersed in a 0.01 M acetic acid/acetate buffer with a pH of 4.7 and the addition of SO_3^{2-} stock to approximately 15 ppm. The pH was measured with a Hanna Piccolo portable pH meter. The samples were allowed to react for approximately 24 hours in the dark.

The samples were analyzed by ion exchange chromatography (IC) to determine the concentration of the anions present. The liquid samples obtained from the filters were passed through a 0.8 μm Nucleopore filter to remove any large particles before injection into the ion exchange column. The ion chromatograph used was a hybrid consisting of a Dionex AS4 analytical column and a Dionex membrane suppressor as the eluent suppressor. The eluent used was 1.6 mM $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer at a flow rate of 2.2 ml/min. The eluting ions were detected with a Waters conductivity detector.

The S(IV) stock was prepared by dissolving Na_2SO_3 salt (BDH Chemicals). It was found there were significant amounts of Na_2SO_4 (7 to 15% by weight) already present, varying from stock to stock. In addition, it was found that the S(IV) stock solution was unstable decomposing at a rate of 10 to 15% per day. As a result, the S(IV) stock solution was made up fresh and calibrated by oxidizing the S(IV) and S(VI) with H_2O_2 and back calculated against sulfate standards.

4. SIMS Analysis

SIMS analysis was carried out using a CAMECA IMS 3f instrument with a O^+ primary beam rastered over a $400 \times 400 \mu$ area while secondary ions for imaging were collected from a central circular spot 250μ in diameter. The primary beam was at a current of 100 nA with 7.5 keV net energy. The filters selected for imaging were those which showed high catalytic activity in the SO_3^- oxidation reaction.

Results and Discussion

The results indicate that specific groups of filters show rapid SO_3^- oxidation to a degree which is significantly greater than that of other filter material. Generally, but not always, the reactive filters are shown by ICP-MS to be rich in metals, especially iron, manganese and nickel. In addition there are groups of filters that show significantly reduced levels of SO_3^- conversion. This latter effect may be due to organics which are preferentially oxidized by dissolved oxygen or to either organic or inorganic chelating agents (i.e. carboxylic acids or phosphates) which chelate metal ions in solution.

Metal ion and metal catalyzed oxidation of S(IV) have been observed to increase oxidation rates, but the exact nature of the interaction is not well understood⁽¹⁾. Such catalysts include iron, manganese, titanium, vanadium, copper and nickel⁽¹⁻⁴⁾. In addition, it is known that graphitic carbon can also catalyze S(IV) oxidation⁽⁸⁾. As well, S(IV) oxidation is believed to be light sensitive⁽⁹⁾.

SIMS imaging⁽¹⁰⁾ can be used to infer the chemical state of various elements on the filter surface. Thus Pb occurs in association with Br, probably the product of automobile exhaust containing Pb and Br from free radical scavengers added to the gasoline. Aluminosilicates can be readily recognized which are either crustal material (wind erosion) or the products of fossil fuel combustion. Interestingly P and F are often associated with the aluminosilicate material. This is suggestive of fertilizer (in the form of phosphate) while F may originate from $\text{Ca}_5(\text{PO}_4)_3\text{F}$ or as a byproduct of aluminium smelting.

Conclusions

The correlation between the metal concentrations and $\text{SO}_3^{=}$ conversion shows that filters with the highest metal concentrations also have the highest conversion. This suggests that the oxidation of S(IV) in the chemical reactivity test in some of these filters is metal catalyzed. More significantly the wide variability in the reactivity of the filter material in contact with $\text{SO}_3^{=}$ solutions shows that the reaction, in concert with IC, can be used to identify air masses which pose significant health hazards either by their direct effects or by the atmospheric chemistry they induce. As well, unusual activity may well be characteristic of the source of the particulate material.

The SIMS results show that ion imaging can be used to elucidate the chemistry of particulate material, which in turn serves as an indication of the source of the material.

References

- (1) M. Conklin, M. Hoffman; "Metal Ion-Sulfur(IV) Chemistry. 1. Structure and Thermodynamics of Transient Copper(II)-Sulfur(IV) Complexes"; *Environ. Sci. Technol.*; 22:8:883-890 (1988).
- (2) J. Kraft, R. Eldik; "The Possible Role of Iron(II)-Sulfur(IV) Complexes in the Catalyzed Autoxidation of Sulfur(IV) Oxides. A Mechanistic Investigation"; *Atmos. Environ.*; 23:12:2709-2713 (1989).
- (3) M. Conklin, M. Hoffmann; "Metal Ion-Sulfur(IV) Chemistry. 2. Kinetic Studies of Redox Chemistry of Copper(II)-Sulfur(IV) Complexes"; *Environ. Sci. Technol.*; 22:8:891-898 (1988).
- (4) M. Conklin, M. Hoffmann; "Metal Ion-Sulfur(IV) Chemistry. 3. Thermodynamic and Kinetics of Transient Iron(III)-Sulfur(IV) Complexes"; *Environ. Sci. Technol.*; 22:8:899-907 (1988).
- (5) L.R. Martin; "Kinetic Studies of Sulphite Oxidation in Aqueous Solution"; *SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations*; J.G. Calvert, Ed.; Butterworth Publishers; Stoneham, MA; 1984.
- (6) C. Clifton, N. Altstein, R. Hule; "Rate Constant for the Reaction of NO₂ With Sulfur(IV) Over the pH Range 5.3-13"; *Environ. Sci. Technol.*; 22:8:586-589 (1988).
- (7) G.S. Taylor, M.B. Baker, R.L. Charlson; "Heterogeneous Interactions of the C, N and S Cycles in the Atmosphere: The Role of Aerosols and Clouds"; *The Major biogeochemical Cycles and Their Interactions*; B. Bolin, R. Cook, Eds.; J. Wiley and Sons, New York, New York; 1983.

- (8) G. Santachiara, F. Prodi, F. Vivarelli; "Absorption of Sulfur Dioxide on Monodisperse Water Droplets and Catalytic Activity of Carbon Particles"; *Atmos. Environ.*; 23:8:1775-1782.
- (9) D. Moller; Kinetic Model of Atmospheric SO₂ Oxidation based on Published Data; *Atmos. Environ.*; 14:1067-1076 (1980).
- (10) R.R. Martin, J.A. MacPhee and K.T. Aye; "SIMS Imaging in the Analysis of Chemically Altered Coal Surfaces"; *Energy Sources*; 11:105-112 (1989).

VOLUME II

SESSION E

ENVIRONMENTAL SOCIO-ECONOMICS RESEARCH

VERBAL PRESENTATIONS

TRADABLE PERMITS FOR THE CONTROL OF SULPHUR OXIDES IN CANADA

BY CHARLES D. MALLORY

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ABSTRACT

In the economic literature, tradable permit systems have been shown to resolve certain environmental problems "efficiently". These are seldom found in practice, however; could such a program be useful for the control of acid rain in Canada? In this paper, the problem of market structure is examined by way of a numerical example involving two large firms. What emerges is that the firms will have different preferences as to the distribution rule. As well, when the market is concentrated, as in Canada, the properties of economic efficiency cannot be guaranteed for régimes based on free distribution of permits to pollutant sources. It is also shown that a zoned emission permit system would appear to be the most useful in the Canadian situation.

RESUME

Dans la littérature économique, il est établi que des programmes de droits d'émissions échangeables puissent résoudre certains problèmes environnementaux de façon "efficace". Cependant, on ne les retrouve pas souvent dans la pratique; est-ce qu'un tel programme pourrait être utile pour le contrôle des émissions acides au Canada? Dans ce papier, le problème de la structure du marché est examiné par le biais d'un exemple numérique impliquant deux grandes firmes. Ce qui sort, c'est que les firmes n'auront pas les mêmes préférences quant à la règle de distribution des permis. Quand il y a peu de firmes polluantes, comme au Canada, il est aussi démontré que la distribution gratuite a peu de chances de respecter les critères d'efficacité économique, si les droits sont distribués gratuitement. Les droits d'émissions par zone s'avèrent les plus utiles dans le contexte canadien.

1 THE BASIC MODEL

A reader familiar with the economics literature relating to environmental problems might find it puzzling that economically efficient tools for the control of pollutants, such as taxes and permits, are hardly used in the real world. The efficiency characteristics of these methods, which imply easier accommodation of growth and incentives to innovate as well as lower costs of control, seem so straightforward that this question deserves greater study.

The object of this paper is to bridge the gap between the theoretical and the practical, making special reference to the problem of sulphur oxides (perhaps the dominant cause of acid rain) in Canada. The aspects of the Canadian situation that are highlighted are the potential dominance of a small number of large emitters and the importance of provincial jurisdiction. Study of the latter question fits well also with the considerable regional disparity in deposition rates.

The theoretical foundations are set out in a simple mathematical model, establishing the standard marginal efficiency conditions on which the economists' case rests. Issues related to market structure are examined using a numerical example involving two firms. Several questions hinge on the initial allocation of permits and their cost. In the last section the regional aspects are discussed.

The economy can be represented by a simple model involving just two nearby firms. The firms have different production processes, for example electricity generation and metal

smelting, thus their cost structures are different. The duopolistic nature of the market for pollution rights in this example is apparent and important, forming the basis of the arguments in the next section; however, the firms are competitive in other factor markets. In the first instance it will be supposed that there are no regulations for the control of atmospheric emissions; a permit market involving a 50% reduction in allowable emissions will then be considered.

E represents the production technology of one firm, which uses a vector of inputs $\mathbf{x} = x_1, \dots, x_n, \dots, x_N$, as well as producing sulphur oxides, denoted by s . This may be presented as

$$E(\mathbf{x}^E, s^E) = 0 \quad <1>$$

Similarly, M represents the technology of the other firm, so that:

$$M(\mathbf{x}^M, s^M) = 0 \quad <2>$$

Firms maximize profits (π) by using inputs in the most efficient combination. The problem of this small "economy" can be solved jointly, using the following Lagrangian expression:

$$\max f = \mathbf{p}(\mathbf{x}^E + \mathbf{x}^M) - \mu [E(\mathbf{x}^E, s^E) + M(\mathbf{x}^M, s^M)] \quad <3>$$

where prices are represented by the vector $\mathbf{p} = (p_1, \dots, p_n, \dots, p_N)$.¹

For any given input x_n , profit maximization implies;

$$p_n = \frac{\delta E}{\delta x_n^E} = \frac{\delta M}{\delta x_n^M} \quad <4>$$

This standard result means that the use of any input x_n should be increased until the value of its marginal product is exactly counterbalanced by its cost. The same is true for smoke: however, as long as no regulatory controls are in force, smoke can be

¹ The price system is relative to the numéraire good, taken to be p_N , which is normalized to one.

generated without incurring costs, so that each firm would produce smoke up to the point where its marginal product is nil, i.e.:

$$\frac{\delta E}{\delta s^E} = \frac{\delta M}{\delta s^M} = 0 \quad <5>$$

The socially optimal solution to this problem would also require equalizing the marginal benefits of controlling smoke generation (mostly reduced damages) to the marginal costs of control of each firm. As before, when the gain in value just equals the expense, this optimal condition is met. This presumes we can evaluate damages from pollution as accurately as we can evaluate the cost of pollution control. In fact, this is a very tricky and somewhat subjective problem. Baumol and Oates (1971) offered a pragmatic solution to the problem, that involves fixing environmental quality targets (that may be varied from time to time) which could then be met at least cost².

Suppose that the government, using a strategy inspired by Baumol and Oates, implements a program of tradable permits, cutting total allowable emissions by half. It calculates emissions without controls, indicated by s_0^E and s_0^M , and issues permits, so that, if D is the total number of permits:

$$D = \frac{1}{2} (s_0^E + s_0^M) \quad <6>$$

Since the firms employ different production technologies, it is improbable that condition <5> could be met if each firm cut its emissions by exactly half. The permits will have a positive price, p_s , and <5> now takes a form similar to the other inputs defined in <4>:

² A dynamic general equilibrium model that permits searching for the optimum may be found in Mallory (1990a).

$$p_s = \frac{\delta E}{\delta s^E} = \frac{\delta M}{\delta s^M} \quad <7>$$

Besides permits, taxes or subsidies could also be used to achieve the efficiency conditions defined by <4> and <7>. Permits have a number of important advantages over alternative mechanisms, which has led to gradually increasing interest in this approach in the context of environmental problems³, namely:

- potentially destabilizing entry conditions do not exist, as new entrants would have to acquire someone else's permits;
- it is a less "noisy" signal when the true form of marginal cost of control and damage functions is uncertain;
- it maintains environmental quality at a specified level; and
- it accomodates new firms and growth of existing firms.⁴

2 A NUMERICAL EXAMPLE

A numerical example will show how firms' interests diverge on the question of the initial distribution. Moreover, the small number of participants breeds market power which can vitiate most of the efficiency gains expected from economic mechanisms.

Each firm's demand for SO₂ emissions as an input can be derived directly from the profit function using Hotelling's Lemma. Using π as the profit function, this demand may be expressed as:

³ It is also, of course, the system which appears to be favoured in the United States. cf. United States of America, (1989), "A Bill to Amend the Clean Air Act ...", which as of this writing had passed in different versions in the House and Senate and had gone to conference.

⁴ These are more fully discussed in Mallory (1990b).

$$s^E = \frac{-\delta\pi^E(p)}{\delta p_s} \quad \text{and} \quad s^M = \frac{-\delta\pi^M(p)}{\delta p_s} \quad <8>$$

Even if all other prices remain constant, outputs of the two firms may vary in response to changing permit prices. We will posit linear demand functions for smoke of the form:

$$\text{Firm E} \quad s^E = 11 (8 - p_s) \quad <9>$$

$$\text{Firm M} \quad s^M = 88 (1 - p_s/3) \quad <10>$$

We can find the price for permits by solving <9> and <10> for p_s and equalizing the results:

$$3 - 3/88 s^E = 8 - 1/11 s^M \quad <11>$$

In that total pollution is to be reduced by half, solving gives:

$$s^E = 24 \quad \text{and} \quad s^M = 64 \quad <12>$$

The equilibrium price of the permits is 2.18 (dollars) at the efficient allocation.

Emission permits may be distributed free or they may be sold; there are numerous intermediate possibilities as well. Free distribution has been justified on the basis of acquired rights to the emissions through historical use, or that the whole of society should pay for changes necessitated by evolving social objectives.

The distributive impact of different régimes emerges both with regard to the cost of pollution control and the cost of permits. Selling the permits by auction raises revenue at the

Table 1

Total Expenses to Firms with Distribution by Auction

	<u>Pollution Control</u>	<u>Cost of Permits</u>	<u>Total</u>
Firm E	69.8	52.4	112.2
Firm M	<u>26.2</u>	<u>139.6</u>	<u>165.8</u>
Total	96.0	192.0	288.0

expense of the polluting firms: this cost is shown for the two hypothetical firms E and M in Table 1. Depending on the shape of the control cost curves and the number of permits available, permit costs may be more or less than the pollution control cost itself. In this example the total cost of permits exceeds total expenses on pollution control, but this need not be so.⁵

2.1 FREE DISTRIBUTION AND DUOPOLY BARGAINING

Granting pollution rights to the firm can be seen as a form of subsidy: whoever gets more permits is the recipient of a larger grant. Yet a variety of different schemes can be described as "equitable", including equi-absolute or equi-proportional reductions in emissions, based on either their original or current values, or equi-marginal cost, to name a few. The last named characterizes a least cost mechanism, while C&C regulations more often focus on emissions.

While different "give away" schemes can have dramatically different effects on individual firms, "the literature provides very little guidance on the consequences of choosing among these various options" (Atkinson and Tietenberg, 1984, p.149). Nevertheless, the government must decide to whom to give the permits. Firms may endeavour to promote the rule that favours them most. Maloney and McCormick (1982) go so far as to say that "at least some firms always benefit from regulation" (at least if they are not being charged for the permits).

⁵ This observation is supported by simulations run by Palmer, Mooz, Quinn and Wolf (1980), Lyon (1982), Hahn and Noll (1983), and Atkinson and Tietenberg (1984).

The strategic interest of firms can be examined in more detail by comparing control expenditures under the "efficient" solution to some other allocation, such as an equal distribution (44 each). The government would in fact have great difficulty determining the efficient allocation a priori.⁹ The firms would have incentive to trade in order to reduce their pollution control expenses. The burden of controlling pollution shifts heavily between the two regimes, showing that the firms are likely to have quite different ideas on which regime is better.

Table 2

Pollution Control Expenses under Different Allocation Regimes

	<u>"Efficient"</u>	<u>Equal</u>
Firm E	69.8	33.0
Firm M	<u>26.2</u>	<u>88.0</u>
Total	96.0	121.0

Firm E may not wish to sell to M, even though it has a financial incentive to do so. Three possible reasons can be given: a large producer might be able to prevent a competitor from locating nearby; a firm might hold on to unused permits anticipating later growth; or, the permit holding company may simply be too preoccupied with other matters to liberate emission permits for the use of others. Thus, any outcome could be considered an equilibrium. Since most acid rain emissions in Canada come from a few sources, the possible concentration of market power in the hands of one or a few firms is a matter of considerable concern.

⁹ Hahn and Noll (1982) argue against attempting to implement the efficient solution as it would result in a thin market.

Thus the problem is not as simple as deciding whether SO₂ generators have acquired rights or not: no regulatory scheme, whether by "command and control", permits, or whatever, can avoid the question of distributional impact on firms. This question emerges more clearly under a permit scheme because the government, having created the permits, has the power to make an initial distribution according to a rule of its choice. The actual costs of control also vary according to the control targets that are set, and this burden is also determined de facto by the government.

When large polluters already held the permits in perpetuity, the efficiency characteristics of the method are jeopardized, and the extent to which these rights are attenuated, the difficulties are reduced. Roberts (1982) argues strongly for permits that "depreciate", that is, are valid for a period of years, after which they expire and must be purchased. Such a method makes it much more likely that the division among firms will ultimately be efficient. Clearly, the sale of permits is less likely to be favoured by industry. As Dewees puts it, "[i]f the political process responds to interest groups that are strongly affected by a policy, the effluent charge and the sale of effluent rights are in deep political trouble unless the revenues are used to compensate the losers."

3 PROVINCIAL JURISDICTION AND REGIONAL INCIDENCE

The limited role that the federal government has defined for itself in environmental problems, and sulphur oxide emissions in particular, relies on its authority to implement international obligations.¹⁰ This was invoked as the justification for the Clean Air Act amendments of 1980, which give it the right to impose a national standard for sulphur oxide emissions. (Whether it will ever do this is another matter.) The federal government has focussed its efforts on conciliating the competing interests of the provinces concerning acid emissions. Thus, in 1987 and 1988 it signed a series of ententes with the seven easternmost provinces, by which they undertake to implement specific cuts in emissions by 1994 (except for Quebec, which gave itself a deadline of 1990).

Transboundary effects can be very significant, and so should be taken into account. Two spatially separate sources will not have the same environmental impact (per unit of emission) as measured at air quality sampling stations, thus one-for-one trades between the firms would not achieve economic efficiency. The direction and turbulence of the winds play a large role, as does the relative concentration of the sources.

Permits may be based either on emissions, usually referred to as an **Emission Permit System** (EPS), or on the impact of the emissions on environmental parameters, generally known as **Ambient Permit Systems** (APS).¹¹ The former type assumes that all emissions have at least approximately equivalent impacts on

¹⁰ cf. Nemetz, 1986.

¹¹ Montgomery (1972) formalized this distinction.

surrounding areas, and emissions are redistributed through trades focusing only on lower cost methods of emission control.

To take spatial location into account, AP trading systems compensate for changes in air quality through transfer coefficients. There are one hundred and fifty monitoring stations in Eastern Canada. For each receptor there would be a separate market, and permits must be held by each source for every receptor site they affect. The problem would be very complex, and it might be impossible to organize any trades at all.

However, when sources are close together, zones can be used to group sources. Using a system of zones, one-for-one emission based trades could be made between sources within a zone. Such a system is a hybrid of the EPS and APS models. In Canada, deposition rates vary much less within individual provinces than across the whole country. Thus provinces (possibly subdivided) might be considered appropriate divisions for zones. This approach dovetails neatly with the extensive jurisdiction that the provinces have. There would be no stringent need for the rules in each province to be identical.

The incentive to trade between zones would emerge with any disparity in permit prices between the two. Trades between zones are tantamount to varying emission ceilings, so that this would involve altering the ceilings that have been established. The terms of trade should be determined by the transfer coefficients, which allow for the difference in deposition rates that sources in each zone are expected to produce. Allowing such inter-zone trades could bring about substantial cost savings without negative impacts on the environment.

4 CONCLUSION

It is often remarked that firms would prefer programmes where permits are given away rather than sold, but differences in firms' cost structures will contribute to different preferences for regulatory intervention. Where market concentration is likely to occur, "give away" permit schemes are not likely to meet the economic objectives that are the raison d'être of such a program. Auctioning the permits would not be affected by this problem, but would likely encounter more determined resistance from industry.

The problems associated with regional diversity appear to be less thorny. Grouping emitters that are close together is not just a simplifying assumption, but one that respects the importance of provincial jurisdiction.

5 REFERENCES

- Atkinson, S.E., & T.H. Tietenberg (1984), "Approaches for Reaching Ambient Standards in Non-Attainment areas: Financial Burden and Efficiency Considerations", Land Economics, 60 (May), pp.148-159.
- Baumol, W.J., and W.E. Oates (1971), "The Use of Standards and Prices for the Protection of the Environment", Swedish Journal of Economics, 73 (March), pp.42-54.
- Deweese, D.N., (1983), "Instrument Choice in Environmental Policy", Economic Inquiry, 21 (January), pp.53-71.
- Hahn, R.W., (1984), "Market Power and Transferable Property Rights", Quarterly Journal of Economics, 99 (November), pp.753-765.
- Hahn, R.W., and R.G. Noll (1982), "Designing a Market for Tradable Permits", in Reform of Environmental Regulation, W.A. Magat (ed.), Ballinger, Cambridge, pp.119-146.
- Hahn, R.W., and R.G. Noll (1983), "Barriers to Implementing Tradable Air Pollution Permits: Problems of Regulatory Interactions", Yale Journal on Regulation, 63 (1), pp.63-91.
- Lyon, R.M., (1982), "Auctions and Alternative Procedures for Allocating Pollution Rights", Land Economics, 58 (February), 16-32
- Mallory, C.D., (1990a), "A Non-tâtonnement Process for an Economy with Water Pollution", PhD thesis, Université de Montréal,
- Mallory, C.D., (1990b), "The Use of Tradable Permits for the Control of Acid Rain in Canada", Environment Canada Contract #KA171-9-7015.
- Maloney, M.T., and R.E. McCormick (1982), "A Positive Theory of Environmental Quality Regulation", Journal of Law and Economics, 25 (April), pp.99-123.
- Montgomery, W.D., (1972), "Markets in Licenses and Efficient Pollution Control Programs", Journal of Economic Theory, 5 (December), pp.395-418.
- Nemetz, P.N., (1986), "Federal Environmental Regulation in Canada", Natural Resources Journal, 26 (Summer), pp.551-608.
- Roberts, M.J., (1982), "Some Problems of Implementing Marketable Pollution Rights Schemes: the Case of the Clean Air Act", in Reform of Environmental Regulation, W.A. Magat (ed.), Ballinger, pp.93-117.
- United States of America, (1989), "A Bill to amend the Clean Air Act to provide for the attainment and maintenance of the national ambient air quality standards, the control of toxic air pollutants, the prevention of acid deposition, and other improvements in the quality of the nation's air", mimeo, 279 pp.

ESTIMATING PUBLIC BENEFITS OF IMPLEMENTING THE PROPOSED REVISIONS TO REGULATION 308

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BACKGROUND

The Ministry of the Environment published a discussion paper on air pollution regulation in Ontario in November, 1987.¹ That document identified problem areas with the existing air pollution legislation and regulations. It went on to propose reforms that would impose direct emission limits on all air pollution sources of any appreciable size. As part of the review process for the proposed revisions to Regulation 308, the Ministry of the Environment commissioned four closely related studies to examine different aspects of these proposed changes.

This study identified the expected air quality, health and environmental benefits to the public from implementation of proposed revisions to Regulation 308. Where possible, these benefits were quantified and valued in economic terms. The study covered 96 contaminants emitted by over 3,500 establishments in 48 industries across Ontario. Benefits were estimated under five scenarios for implementation of the proposed revisions.

ANALYTICAL FRAMEWORK

The study was an ambitious attempt to grapple with a problem at the frontiers of industrial chemistry, health risk analysis and economics. The public benefits of reduced contaminant emissions depend upon:

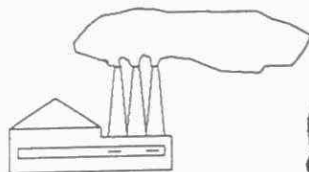
- the contaminant whose emissions are reduced;
- the change in concentration of that contaminant at each point;
- the population and environmental resources in the areas where concentrations are reduced; and
- the human health and environmental responses to the reduced concentrations.

Figure 1 illustrates the problem of identifying and estimating benefits. It shows a source of contaminant emissions that would be affected by the proposed revisions. For most contaminants there are other sources that would not be affected by Regulation 308. These include motor vehicles, forests (a major source of some types of hydrocarbon gases), point sources governed by other regulations, sources too small to be affected by Regulation 308 and emissions that come from outside the province.

The proposed revisions to Regulation 308 would reduce the emissions from specified sources, and this would reduce the ambient concentration in the area surrounding the

¹ Clean Air Program, Stopping Air Pollution At Its Source, Discussion Paper, Air Pollution-General Regulation, (Regulation 308), Ministry of the Environment, November 1987.

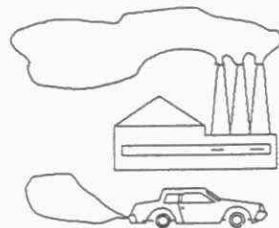
THE ANALYTICAL PROBLEM



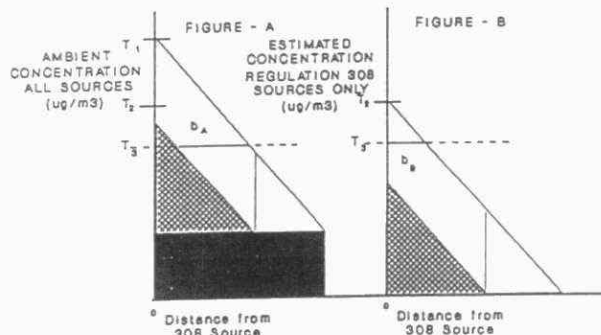
REGULATION 308
CONTAMINANT
EMISSIONS



RESOURCES



NON-REGULATION 308
CONTAMINANT
EMISSIONS



LEGEND:

- - Present Concentration Non 308 Sources
- ▨ - Proposed 308 Source Concentration
- - Reduction in 308 Source Concentration

source, assuming that emissions from other sources did not change. The change in ambient concentration can be estimated from the change in emissions from Regulation 308 sources. However, the level of ambient concentration of a given contaminant cannot be determined without knowing the emissions from all non-Regulation 308 sources. These emissions are usually not known.

EMISSIONS SOURCES

A list of economic sectors suspected to emit one or more of the 96 Regulation 308 contaminants was developed in consultation with the Ministry of the Environment and the consultants responsible for the related studies. The starting point was the activities or processes, such as whey drying, painting of automobiles, or incineration of hospital wastes, believed to generate one or more of the contaminants of interest. The activities and processes of interest were linked to SIC Standard Industrial Classification categories so that the technical and economic information collected and organized on that basis could be used. In many cases the correspondence was very good, in other sectors the analysis was limited to part of an SIC industry; and in a few cases, such as hospital, municipal and industrial incinerators, we simply defined the sector to suit our purposes.

We used two principal sources to identify locations and sizes of establishments in each sector. These sources are:

- the Made in Ontario data base compiled by the Ontario Ministry of Industry, Trade and Technology; and
- a listing of establishments purchased from Statistics Canada.

EMISSIONS BY SOURCE

The emissions data were supplied by Senes Consultants Ltd. They provided estimated annual emissions by contaminant for each economic sector under the present regulations and under the five scenarios for implementation of the proposed revisions to Regulation 308. We adjusted these data in several ways to meet the needs of our analysis:

- the emissions had to be apportioned among the individual sources in the sector;
- the capacity utilization assumed had to be changed;
- the emissions rate had to be changed from tons per year to grams per second; and
- the composite categories of PM and VOC's had to be disaggregated into their constituent chemicals.

Total emissions for the sector were apportioned among the individual establishments in the sector on the basis of the selected measure of size, usually employment. The emissions were adjusted to reflect capacity utilization. Senes estimated emissions at full capacity, but benefits occur only as a result of changes to actual emissions. Hence, emissions were scaled to actual capacity utilization for the industry. Finally, the emissions rate was converted from tonnes per year to grams per second assuming continuous operation.

rate was converted from tonnes per year to grams per second assuming continuous operation.

One of the challenges in this project was to disaggregate PM and VOC's emissions into their individual chemical constituents. Reduced emissions of particulate matter, regardless of the composition, can yield health (respiratory problems, eye irritations etc.) and other (soiling, visibility reduction) benefits. But most health and environmental benefits derived from reduced emissions of PM's and VOC's result from lower concentrations of specific chemicals. Thus, the composition of the VOC and PM emissions had to be determined so that the changes in emissions of specific chemicals can be examined. This was done using U.S. data on the composition of PM and VOC emissions for various processes.

DISPERSION MODELLING

When a contaminant is emitted by a source, it is dispersed over the surrounding area. A dispersion model was used to calculate annual average ambient concentration attributable to the emissions from each source. The Ministry of the Environment's new dispersion models developed for use with Regulation 308 were used for the analysis. These models cover an area 24 km in each direction from the source.

We used a "pre-public-release" version of the Ministry's GAS model for the dispersion modelling. The climatological data it requires as input include both surface observations and upper air observations. There is no single station in the southern part of Ontario that has all of the information needed. On the basis of similarity of weather conditions and proximity to Regulation 308 emission sources, fourteen Ontario weather stations were selected to represent weather conditions across the province. A representative year was identified, U.S. or Quebec upper air observations were matched to each station and the dispersion pattern calculated for each of these fourteen stations.

To precisely model emissions from such sources the exact dimensions of the building and the stack must be known. For this study, no information was available on building or stack dimensions for any source. To estimate ambient concentration, each source was assumed to be a building of 7 m height and 100 m width with a stack of less than 14 m elevation, emitting pollutants at 0 velocity and at ambient exit temperature. Such a building is a typical "industrial park" source.

Subsequently, the simplifying assumption that all stack characteristics were similar was dropped. Instead, for each industry detailed stack characteristics and emissions data for a stratified sample of establishments were applied to the industry as a whole. The resulting emissions data were then used to re-estimate the total benefits associated with revisions to Regulation 308.

AMBIENT CONCENTRATIONS

Many of the contaminants studied are also emitted by sources other than the specified industries. To calculate benefits it is sometimes necessary to know the change in the

ambient concentration from all sources likely to occur as a result of implementation (in respect of some sources) of the proposed revisions to Regulation 308.

Of the 96 contaminants considered, monitoring data are available only for cadmium, chromium, lead, manganese, nickel, sulphur dioxide, PM and total VOC's. The monitoring data are point data, i.e., ambient concentrations at the monitoring station locations. Using the dispersion modelling results, we determined the concentration of a monitored contaminant from Regulation 308 sources at each monitoring station. We subtracted this concentration due to Regulation 308 sources from the ambient concentration at the monitoring station. The result was a "residual" value for ambient concentration of the contaminant due to non- Regulation 308 sources at each monitoring station.

Not surprisingly, this subtraction did not lead to uniform "residual" figures at all monitoring stations. For each contaminant, except sulphur dioxide, we added the maximum "residual" value from all monitoring stations to the estimated concentration due to emission from Regulation 308 sources. This maximum residual was added to the concentration due to Regulation 308 source emissions under existing regulations, and under each implementation scenario for the proposed revisions to Regulation 308. The result was an upper bound estimate of total ambient concentration of the contaminant at all relevant points.

EXPOSURE - RESPONSE FUNCTIONS

The relationship between the exposure to a contaminant and the consequent damage is called an exposure-response function. Profiles were assembled for each contaminant, summarizing known effects, relevant standards and exposure-response functions where available.

Exposure-response functions were identified for carcinogenic or suspected carcinogenic contaminants. Functions were also available for some non-carcinogenic contaminants which have effects on health; nitrogen dioxide, sulphur dioxide and particulate matter. Functions for visibility effects and damage to materials were available for nitrogen dioxide and particulate matter.

It should be noted that the absence of an exposure-response function does not mean that health or other effects will not occur, only that their magnitude cannot be estimated at present. Furthermore, it should be recognized that the approach taken to benefit estimation, based on measurable benefits within a single year, did not allow for damages resulting from the bio-accumulation of toxic chemicals.

RESULTS

Some of the principal known sources of damage to other environmental resources, such as ozone, nitrogen dioxide and sulfates play a relatively minor role in this assessment. The largest sources of nitrogen dioxide and sulphate emissions fall under the acid rain

initiative and hence outside the purview of this analysis. Ozone was not addressed in this study either, because it is formed in the atmosphere rather than emitted.

Cancer Mortality

Many of the 96 contaminants analyzed are suspected, probable or known carcinogens. Cancer unit risk factors are available for 20 of those contaminants. These enabled estimates to be made of the reduced risk to cancer mortality resulting from the proposed revisions to Regulation 308, as shown in Table 1. A reduction in death due to cancer of ten to seventeen people per year can be expected from reduced exposure to arsenic, chromium and nickel. Reduced exposure to other cancer causing contaminants were found to be insignificant with respect to mortality.

Non-Cancer Mortality

Exposure-response functions for estimating the reduction in non-cancer deaths resulting from lower contaminant emissions are available for sulphur dioxide and particulate matter only. The estimated reductions are shown in Table 1. The reduction in non-cancer mortality is roughly four times the reduction in cancer mortality.

Table 1 Estimated Reduction in Annual Mortality by Contaminant and Scenario
A & D B C E
(to 2003)

Cancer				
1,3 Butadiene	1.0	1.0	1.0	1.0
Arsenic	7.0	8.0	6.0	7.0
Chromium	8.0	8.0	4.0	8.0
Nickel	0.5	0.5		0.5
Subtotal				
Cancer	17	18	11	17
Non-Cancer				
Sulphur dioxide	56	70	19	19
Particulate matter	11	12	5	8
Subtotal non-cancer	67	82	24	27
Total Reduced Mortality	84	100	35	44
Estimated Value (million 1986 \$C)				
low	\$184.8	\$220.0	\$77.0	\$96.8
central	\$583.8	\$695.0	\$243.3	\$305.8
Source DPA (1988, 1989)				

Reduced Morbidity

Exposure-response functions for health benefits due to reduced morbidity are available for sulphur dioxide and particulate matter. The estimated human health benefits resulting from reduced emissions of these contaminants are shown in Table 2.

Table 2: Estimated Reduction in Annual Morbidity by Contaminant and Scenario

	A & D	B	C	E
Sulphur Dioxide				
Hospital admissions for respiratory disease	136	171	45	47
Hospital days for respiratory conditions	1,341	1,686	448	460
Value (million 1986 \$C)				
low	\$0.9	\$1.2	\$0.3	\$0.3
central	\$3.1	\$3.9	\$1.0	\$1.1
Particulate Matter				
Emergency room visits	637	681	321	492
Restricted activity days	133,500	142,500	67,000	103,000
Value (million 1986 \$C)				
low	\$1.4	\$1.5	\$0.7	\$1.1
central	\$8.2	\$8.7	\$4.1	\$6.3
Total				
(million 1986 \$C)				
low	\$2.3	\$2.7	\$1.0	\$1.4
central	\$11.3	\$12.6	\$5.1	\$7.4

The benefits from reduced sulphur dioxide emissions consist of reductions in hospital admissions and the number of hospital days for respiratory conditions. Benefits from reduced particulate matter emissions consist of reductions in emergency room visits and restricted activity days.

Reduced Exposures to Concentrations Above the Proposed Standards

The estimates of human health benefits summarized in Tables 1 and 2 only capture a part of the human health benefits from more stringent control emissions required to meet the proposed revisions to Regulation 308. Exposure-response functions have yet to be developed for the majority of contaminants examined.

In the absence of an exposure-response function, the analysis examined the population exposed to contaminant concentrations above the standard included in the proposed revisions. In the case of cadmium, chromium, lead, nickel and sulphur dioxide, where monitoring information was available, the analysis was based on the estimated ambient concentration (from all sources). For the other contaminants, however, the analysis was limited to exposure to the concentrations estimated from Regulation 308 source emissions alone. In those cases, they underestimate the public benefits of the proposed revisions to Regulation 308.

Table 3 summarizes the estimates of population exposed to concentrations of contaminants above the proposed ambient standards. Eleven contaminants were estimated to be at above-standard levels at the estimated emission levels in 1987. The revisions to Regulation 308 under all scenarios would significantly reduce the population exposed to concentration levels above the proposed standards.

The analysis was based on annual average concentrations, the dispersion of these contaminants was been modelled on the assumption that they are gases, and the smallest area considered was 16 km². Hence the analysis did not detect concentrations above the proposed standard if they occur in smaller areas, especially near the emission sources, or over shorter periods.

Materials Damage

Functions for estimating reduced damage to materials are available for nitrogen oxides and particulate matter. These functions are expressed in terms of the dollar value of materials damage per unit change in ambient concentrations. Consequently, they cannot be used to estimate the reduction in damage measured in physical units, such as the reduced frequency for painting or the increased longevity of materials. Table 4 shows that the estimated benefits from reduced damage to materials are mostly attributable to the reduction in nitrogen oxides.

Visibility Benefits

As with the reduction in materials damage, the functions available for estimating the value of improved visibility are expressed directly in dollar terms and do not permit benefit estimates to be made in physical units. These functions, which were derived from

Table 3 Estimated Population Exposed to Above-Threshold Concentrations of Contaminants (000's)

	Current	Scenarios	Scenario	Scenario	Scenario
		A & D	B	C	E
Arsenic	228	34	34	67	34
Cadmium*	**	-	-	-	-
Chromium*	75	26	26	34	26
Ethylene Dibromide	345	-	-	-	345
Fluorides	**	-	-	-	-
Lead*	12	-	-	-	-
Nickel*	34	-	-	-	-
Nitrogen Oxides	1	1	1	1	1
Silica	645	129	83	288	238
Sulphur Dioxide	67	**	**	12	12
Suspended Particulates	159	22	**	95	45

- Notes:
- * Denotes contaminant for which population exposure is based on ambient concentration from all sources. In all other cases exposure is to concentrations due to Regulation 308 Source emissions alone.
 - ** Population exposed is less than 500.
 - Exposure levels are negligible.

studies of the value of changes in visibility in California, yield extremely high estimates for the value of improved visibility when applied to the emission reductions considered in this assessment. These high values are due, in part, to the inability of the exposure-response function to distinguish between proportionately large improvements in areas where existing visibility is low, and those where visibility is relatively high. In the latter case, observed visibility increases due to reductions in particulate emissions could be very small, yet would be given the same monetary value as equal percentage reductions in areas where visibility is originally very poor. For this reason the benefits were omitted from the report.

Odour

Five of the 96 contaminants and emissions from restaurants are considered to be potential odour problems. This assessment indicates that hydrogen sulphide, trichloroethylene and restaurants all satisfy the standards proposed as part of the revisions to Regulation 308.

Phytotoxicity

Only eight of the 96 contaminants were identified as being potentially harmful to plants: cadmium, chlorine, ethylene, hydrogen chloriden, nickel, selenium, and sulphur dioxide.

At present only very small areas are exposed to concentrations in excess of the proposed standards for these contaminants. Hence, the public benefits in the form of reduced damage to crops and forests resulting from the proposed revisions are negligible.

AGGREGATE ECONOMIC VALUATION

The estimated value of reduced mortality and morbidity and of less damage to materials resulting from implementation of the proposed revisions are summarized in Table 5.

These figures apply only to those few cases where the public benefits can be quantified and the associated economic value can be estimated. The absence of a damage function or even emissions data for a contaminant does not mean that there is no benefit to be had by regulating emissions of that contaminant. Given the limited range of contaminants and benefits that can be quantified and valued, the figures in Table 5 should be considered minimum estimates of benefits.

Annual benefits range from \$300 to \$625 million (1986 C\$) in the low case and from \$725 to \$1,525 million in the central case. Health benefits account for 25 to 35 percent of the total in the low case and 35 to 45 percent of the total in the central case. The least stringent scenario (C) yields the lowest benefits and the most stringent (B) produces the highest benefits.

REVISED PROPOSALS

Revised proposals to reform to Ontario Regulation 308 under the Environmental Protection Act were issued for comment on August 16, the proposals are the centrepiece

Table 4: Estimates of Benefits From Reduced Damages to Materials by Scenario (million 1986 \$C)

	A & D	B	C	E
Nitrogen oxides				
Low	\$333.2	\$402.9	\$234.7	\$279.7
Central	\$666.3	\$805.8	\$468.8	\$559.4
Particulate matter				
Low	\$1	\$1	\$1	\$1
Central	\$18	\$19	\$9	\$14
Total				
Low	\$334.2	\$403.9	\$235.7	\$280.7
Central	\$684.3	\$824.8	\$477.8	\$573.4

Table 5: Aggregate Amounts of Benefits to Which an Economic Value Has Been Assigned (Millions of 1986 \$C Annually)

	A & D	B	C	E
Low Cost				
Reduced mortality	\$184.8	\$220.0	\$77.0	\$96.8
Reduced morbidity	\$2.3	\$2.7	\$1.0	\$1.4
Lower materials damage	\$334.2	\$403.9	\$235.7	\$280.7
Total	\$521.3	\$626.6	\$313.7	\$378.2
Central Case				
Reduced mortality	\$583.8	\$695.0	\$243.3	\$305.8
Reduced morbidity	\$11.3	\$12.6	\$5.1	\$7.4
Lower materials damage	\$684.3	\$824.8	\$477.8	\$573.4
Total	\$1,279.4	\$1,532.4	\$726.2	\$886.6

of the province's Clean Air Program, designed to reduce atmospheric emissions from stationary sources. The requirements will affect an estimated 20,000 emitters. The draft regulation requires:

- that all significant stationary sources of emissions to the atmosphere to be controlled to minimize releases to the environment;
- controls commensurate with the known or suspected hazard of the contaminant being emitted, with the strictest controls on emitters of substances known to have serious health and environmental effects (toxics), especially those which persist, accumulate in living things and have the ability to cause cancer or mutate genes;
- that all significant (new and existing) sources of emissions to the atmosphere must have a certificate of approval, renewable on a ten-year basis, to operate; and
- that community air standards be met throughout the province.

To achieve these aims the Clean Air Program proposes:

- systems for classifying contaminants according to their potential to impact the environment;
- a three-level system of emission control requirements which will be linked to the classification system to ensure appropriate controls;
- requirements for Certificates of Approval to construct and operate, with the operational part renewable every ten years;
- provisions to require the use of state-of-the-art computer models or their equivalent to estimate the impact of proposed emissions on existing community air quality;
- a process for reviewing the current single source point of impingement standards and converting them to ambient air standards, and to produce new standards as the need arises;
- revisions to the existing procedures concerning the granting of air approvals;
- a phasing-in mechanism based on the contaminant evaluation scheme;
- monitoring and quality assurance requirements.

A six-month comment period has been established for the regulatory proposal.

Recycling, Reducing and Reusing: A Theoretical Framework
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1.0 INTRODUCTION

Macroeconomic models are generally based on a particular national income accounting framework. The current approach treats waste and pollution generation in such a way that any increase in these activities increases directly the GDP of the economy. Thus, a society can increase its GDP by simply increasing the waste it produces. This follows from the fact that pollution abatement and sewage treatment activities appear as part of the final demand of the economy. Carbage collection and sewage treatment are part of the municipal government sector and this sector, like all other government activity, is treated as if it produces final output. Common sense suggests that no society should be considered richer or better off if it were to produce more waste. Since the current GDP measure does exactly this, it appears sensible to re-examine the GDP concept and the way it is measured.

In this study we present a suggested reformulation of the accounting framework so as to treat waste management and pollution abatement as services to business whose costs should be charged against business revenues. Even such services to households may be considered as costs of output to the extent that part of household activity may be incorporated within the business sector. In this way they appear as a cost to society and not as final output.

The major contribution of the study, however, is the new theoretical framework that is developed to correspond to the new reformulated accounting framework. Within this new framework it is possible to identify clearly and

Carefully the recycling activity and the operations of waste management. The rectangular input output framework is particularly suited for this treatment as it allows different industries to produce the same output, and identifies different commodities as inputs in the production of the same output. In this way paper can be made from virgin pulp or from recycled paper. The two industries use different technologies but produce the same output. Several new commodities are also introduced into the system. These include recyclables and recycled commodities. What in the past was waste and disposed of is now a new input into the production of consumables. Recyclables are produced primarily but not exclusively by households and institutions, and are used by the recycling industry to produce products that are almost indistinguishable from virgin products.

The new framework extends our ability to deal with environmental and waste management issues that are difficult or impossible to deal with within the old framework. The "throwaway society" such as the one we have in Canada produces about 1.7 kgs per person per day. This is the highest per capita waste production in the world. Ontario alone produced about ten million tonnes of waste in 1987, this is more than one tonne for every person. Waste volumes are increasing at very rapid rates. Over the past decade the per capita waste generation rate exceeded 25 percent. As a result, landfill sites in high growth areas such as Metro Toronto have experienced bottlenecks. Over 160 landfills in the province have less than two years of approved remaining capacity.

With the new framework, it is possible to examine the socioeconomic consequences of increased use and production of recyclables. Equally important

is our ability to assess the relative efficiency of alternative policies to reuse or reduce the use of products and resources through price incentives and full cost charges.

2.0 The Model

Recycling, reusing and waste management activities involve the use of scarce resources and the generation of outputs and services. Typically, these activities were either neglected, misallocated or subsumed within other activities of other sectors within the standard input output accounting framework. Any attempt to focus on these activities calls for a major reformulation of the standard accounting framework. The adjustment process involves not only broadening the use, make and final demand matrices of the rectangular input output framework to encompass new commodities and industries, it also calls for redefining of the accounting relationships governing the system.

2.1 The Modified Use Matrix

The standard use matrix is extended to include explicitly sorting station activities, recycling and waste disposal activities. These industries use resources and generate value added. The commodity set is also expanded and disaggregated to show explicitly scrap, recyclables, recycled products and waste treatment and disposal services. Table 1 presents the modified structure of the use and final demand matrices that reflect the expanded industry and commodity spaces.

Table 1

The Modified Use and Final Demand System

Industries Commodities	1	2	S	R	W	H	G	E	M	Q
Composite 1	U_{11}	U_{12}	U_1S	U_{1R}	U_{1W}	H_1	G_1	E_1	$-M_1$	q_1
Paper 2	U_{21}	U_{22}	U_2S	U_{2R}	U_{2W}	H_2	G_2	E_2	$-M_2$	q_2
Recyclable paper 3	0	0	U_3S	U_{3R}	U_{3W}	H_3	G_3	E_3	$-M_3$	q_3
Recyclable composite 4	0	0	U_4S	U_{4R}	U_{4W}	H_4	G_4	E_4	$-M_4$	q_4
Scrap 5	U_{51}	0	U_5S	U_{5R}	U_{5W}	H_5	G_5	E_5	$-M_5$	q_5
Waste Management 6	U_{61}	U_{62}	U_6S	U_{6R}	0	H_6	G_6	E_6	$-M_6$	q_6
Recycled Products 7	0	U_{72}	0	0	U_{7W}	0	0	E_7	$-M_7$	q_7
Value Added	VA_1	VA_2	VA_S	VA_R	VA_W	VA_H	VA_G			Y
Gross Output $Y+\delta q$	g_1	g_2	g_S	g_R	g_W	H	G	E	$-M$	

A number of interesting characteristics are embedded within Table 1 that reveal the nature of the modifications suggested.

First, a strong distinction is made between recyclables and recycled products. Recyclables are gathered, sorted and delivered either to the primary industries or to the recycling industry.

Second, recycled products are either delivered as outputs to final demand or as inputs to primary industries.

Third, waste disposal services are allocated to businesses and to households. Deliveries to businesses appear as deliveries to intermediate

demand. In the standard input output system waste disposal services are allocated entirely to final demand. This reallocation implies reducing the value of net output of the economy. In addition, charges paid by businesses for waste disposal services reduces their operating surplus and therefore the value added assigned to them. These charges appear as revenues of the waste disposal industry and raises its value added. Thus, two changes result from this adjustment. Net output of the economy is changed by moving a part of the deliveries of this activity from final demand to intermediate demand, and also the distribution of value added between industries.

2.2 The Modified Final Demand Matrix

Exporting and importing recyclables, recycled products and waste are allowed explicitly into the framework. Maintaining balance between supply and demand for these products is likely to be difficult particularly in the initial stages of production. Thus imports and exports of surpluses and short falls are likely to play prominent roles in sustaining the operations of these activities. Furthermore, final demand sectors are users as well as producers of recycled and recyclables. Their activities and choices will influence in a significant way the operations and activity levels of these sectors.

2.3 The Modified Make Matrix

The extension and expansion of the use matrix impose several modifications to the make matrix. Some of these changes include:

First, recyclables are primarily produced by all sectors including some final demand sectors.

Second, paper produced from virgin inputs is indistinguishable from paper produced from recycled paper.

Third, waste management services are produced solely by the waste management industries.

Fourth, recyclables are transformed into recycled products at sorting stations or at recycling industries.

Table 2
The Modified Make Matrix

Commodities Industries	1	2	R _p	R _C	R _S	6	7	Industries
1	V ₁₁	0	V ₁₃	V ₁₄	V ₁₅	0	0	g ₁
2	0	V ₂₂	V ₂₃	V ₂₄	V ₂₅	0	0	g ₂
S	0	0	0	0	0	0	V _{S7}	g _S
R	0	0	0	0	0	0	V _{R7}	g _R
W	0	0	0	0	0	V _{W6}	0	g _W
H	0	0	V _{H3}	V _{H4}	V _{H5}	0	0	R _H
G	0	0	V _{G3}	V _{G4}	V _{G5}	0	0	R _G
Commodities	q ₁	q ₂	q ₃	q ₄	q ₅	q ₆	q ₇	δ

Several features define the modification's to the structure of production presented in Table 2. They include: first, recyclables are produced by all sectors other than the sorting and recycling industries. Second, the paper industry produces paper from Virgin materials and recycled materials. Third, recyclables are transformed into recycled products by the sorting stations and the recycling industries. Fourth, households and governments are treated here as producing sectors of recyclables.

2.4 The Equations of the Model

The model has several components. We begin with the material balances: For i , we have

$$(1) \quad U_{i1} + U_{i2} + U_{iS} + U_{iR} + U_{iW} + H_i + G_i + E_i - M_i = q_i$$

In more compact form

$$(2) \quad \sum_j U_{ij} = \sum_s l_{is} = q_i$$

$j = 1, 2, S, R, W$

$s = H, G, E \text{ and } M.$

when

i_{ij} : is the delivery of commodity i used in industry $J.$

l_{is} : is the delivery of commodity i with final demand category $S.$

The matrix defines the following relationships:

For Commodities:

$$(3) \quad q_1 = v_{11}$$

$$(4) \quad q_2 = v_{22}$$

$$(5) \quad q_3 = v_{13} + v_{23} + v_{H3} + v_{G3}$$

$$(6) \quad q_4 = v_{14} + v_{24} + v_{H4} + v_{G4}$$

$$(7) \quad q_5 = v_{15} + v_{25} + v_{H5} + v_{G5}$$

$$(8) \quad q_6 = v_{W6}$$

$$(9) \quad q_7 = v_{57} + v_{R7}$$

For Industries:

$$(10) \quad g_1 = v_{11} + v_{13} + v_{14} + v_{15}$$

$$(11) \quad g_2 = v_{22} + v_{23} + v_{24} + v_{25}$$

$$(12) \quad g_S = v_{S7}$$

$$(13) \quad g_R = v_{R7}$$

$$(14) \quad g_W = v_{W6}$$

$$(15) \quad R_H + v_{H3} + v_{H4} + v_{H5}$$

$$(16) \quad R_G + V_{G3} + V_{G4} + V_{G5}$$

The Use matrix defines the following set of relationships

$$(17) \quad q_i = \sum_j \delta_{ij} u_j + VA_i \quad i = 1, 2, S, R, W$$

and

$$(18) \quad H = H_1 + H_2 + H_3 + H_4 + H_5 + H_6 + VA_H$$

$$(19) \quad G = G_1 + G_2 + G_3 + G_4 + G_5 + G_6 + VA_G$$

$$(20) \quad E = E_1 + E_2 + E_3 + E_4 + E_5 + E_6 + E_7$$

$$(21) \quad M = M_1 + M_2 + M_3 + M_4 + M_5 + M_6 + M_7$$

Equations (1) through (21) are accounting identities. The following hypotheses are tendered to operationalize the model.

$$(22) \quad I_{ij} = \bar{I}_{ij} g_j \quad j = 1, 2, S, R, W$$

Commodity input use is proportional to industry output.

$$(23) \quad H_i = h_i \bar{n}$$

Consumption by commodity depends on the proportion of labour income devoted to consumption.

$$(24) \quad \bar{n} = cLI$$

Labour income is the sum of wages and salaries, "c" is the average propensity to consume.

$$(25) \quad G_i = g_i G$$

Government expenditure by commodity is determined by constant shares "g_i".

$$(26) \quad E_i = E$$

Exports by commodity are determined exogenously.

$$(27) \quad M_i = m_i (M_i + q_i) \quad i = 1, 2$$

Commodity imports of the composite good and paper are proportional to total

supply.

$$(28) \quad M_i = M_i \quad i = S, R, W$$

Other imports are exogenously determined.

$$(29) \quad V_{ji} = V_{ji} q_i$$

The share of industry "j" is the production of commodity "i" as fixed by the existing market share coefficient V_{ji} .

Several additional restrictions on policy specifications may be postulated to simulate their effects on the economy's performance. For, example we may hypothesize the following:

$$(30) \quad \begin{aligned} H_4 + V_{H3} &= S_H = {}_H H \\ H_4 &= sh_4 S_H \\ V_{H3} &= sh_3 S_H \\ G_4 + V_{G3} &= S_G = {}_G H \\ G_4 &= sg_4 S_G \\ V_{G3} &= pg_3 S_G. \end{aligned}$$

The parameters sh_i and sg_i reflect the household and government recycling participation rates. Blue box programmes ultimately raise the values of these coefficients and allow model users to simulate the impact of such policies on waste disposal.

THE ECONOMIC IMPLICATIONS OF THE ZEBRA MUSSEL (*Dreissena polymorpha* Pallas)
INVASION OF THE GREAT LAKES

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ABSTRACT

Various authorities and media reports have cited dollar values of the current or potential damages caused by the zebra mussel or of its control ranging from \$3.7 billion to \$5 billion for establishments on both sides of the Great Lakes over the next 10 years. The actual damages and adverse effects caused by the zebra mussel in Ontario and the monetary values and other economic implications associated with them are presented in this paper along with estimates of the monetary values of potential responses to the key adverse effects caused by the animal in Ontario and the potential economic implications of these consequences.

To date, at least 14 biofouling cases have been reported in Ontario. Capital and other one-time expenditures directly attributable to these cases amount to about \$8.7 million. Ontario industrial establishments and power plants on the Great Lakes have so far been spared the extreme consequences of equipment damage and plant shut-downs. Potential costs of preventative measures in 8 Ontario Hydro power plants, 86 municipal water treatment plants and 67 industrial plants which use Great Lakes water directly amount to about \$164 million for equipment and installations, \$7.6 million per year for operating and chemical costs, \$1.25 million each year for cleaning and removal and \$2.25 million per year for monitoring activities. Ontario Hydro also intends to devote about \$3.5 million in research over the next 3 years.

Application of an Ontario beach use model indicates that, in 10 beaches on Lake Erie currently infested with zebra mussels, beach use occasions could be reduced by as much as 18% if the effects caused by zebra mussels only partially reduced the attractiveness of the locations. However, if the adverse effects are perceived by people to be of major importance, beach attendance would be reduced by as much as 50%.

It is tentatively concluded that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. Increased monitoring and surveillance would be one of the best investments that can be made at this time.

1. INTRODUCTION

In only 2 years since it was first observed in Lake St. Clair, the zebra mussel (*Dreissena polymorpha* Pallas) has become a major problem for communities and industrial plants that line the shores of Lakes Ontario, Erie and Huron. A native of fresh water lakes in central Europe, larval forms of *Dreissena* were probably brought to the North America in the fresh water ballast of ships. Here in the Great Lakes, zebra mussels have found ideal conditions for reproduction, rapid growth, development of dense colonies (called *druses*) and wide dispersion.

Although individual mussels grow no larger than the size of a fingernail, they can cause serious biofouling in municipal and industrial water systems and unwholesome accumulations of shells on recreational beaches and shorelines. While all of the potential effects of the zebra mussel are not entirely detrimental, biofouling and other adverse consequences have dominated media reports.

Quantitative measures of the present and potential bio-physical impacts of the zebra mussel are of interest and importance to program development. However, the monetary values associated with these effects are needed to judge their importance to individuals and, with certain qualifications, to society as a whole. Value information is particularly important if both beneficial and adverse effects are involved. Estimation of the monetary values associated with a particular environmental problem or issue helps to determine how much

money and effort ought to be allocated to a specific resolution activity such as zebra mussel control, clean-up and prevention of biofouling. Such estimates are also required in order to assess the broader economic implications that can result from these consequences.

Various authorities and media reports have cited dollar values of the current or potential damages caused by the zebra mussel or of its control. These values range from \$3.7 billion for establishments on both sides of the Great Lakes over the next 10 years (Stanley, ca. 1990), "...\$4 billion by the end of the decade... ..Billions more likely will be needed in the next century." (Geigen-Miller, Oct. 6, 1990) to \$5 billion over the next decade (Toronto Star, Aug. 9, 1990). Attempts to verify and trace the sources of these estimates have revealed unclear methodologies, misquotes or lack of documentation.

Thus, while much valuable information about the biology of *Dreissena polymorpha* and the technologies of controls are being accumulated, little if any systematic work on the economic implications of the zebra mussel invasion of the Great Lakes is under way. The present study is intended to fill this apparent gap and assess the financial and economic ramifications of the zebra mussel in Ontario.

The primary purposes of this study are to:

- 1) present a documented accounting of the actual damages and adverse effects caused by the zebra mussel in Ontario and the monetary values and other economic implications associated with them, and
- 2) prepare documented estimates of the monetary values of potential responses to the key adverse effects caused by the zebra mussel in Ontario and the potential economic implications of these consequences.

2. PLAN OF PAPER

The present paper is a distillation of a more extensive reference report prepared by the authors (Donnan & MacKay, forthcoming). More details on each of the issues discussed here can be found in that reference.

In the next Section, steps and procedures that will be utilized to produce the relevant estimates are presented. This is followed in Section 4 by a brief description of the biological characteristics of the organism and an enumeration of potential effects on human structures and activities. Relevant data on the areas of current and potential infestation on the Canadian side of the Great Lakes are noted in this Section as well.

Methods and technologies which have been applied, and are being studied, to remove or prevent zebra mussel infestations are summarized in Section 5. Locations at which the zebra mussel has actually caused damages or has induced expenditures on clean-up or prevention are listed in Section 5. Estimates of the monetary values associated with different types of response activities (ie. cleaning of pipes vrs preventative installations) in various sectors (eg. electric power generating stations, municipal water treatment) are presented in Section 6.

Potential effects of zebra mussel shell littering on recreational beaches are discussed in Section 7.

Section 8 reviews the experience and effects of other biological invaders of the Great Lakes, particularly the predatory sea lamprey (*Petromyzon marinus*).

Findings and conclusions are found in Section 9.

3. PROCEDURES AND METHODOLOGIES

An assessment of the economic implications of any environmental or natural resource phenomena begins with information on the biophysical nature of the problem and the mechanisms by which human activities and perceptions are affected. When the relevant biophysical and human interrelationships are identified and quantified to the extent possible, data on the populations, resources, locations or facilities at risk

must be assembled. These data are used to "scale up" the physical, spatial and economic dimensions of the effects in question.

A third step involves positing different scenarios that define potential human responses to the adverse (or beneficial) effects that are of concern. Human responses to the environmental issue at hand may involve the allocation of various types of natural and man-made resources to repair, replace or avoid adverse effects or they may involve the reduction in the utility and enjoyment of specific activities or natural assets because of the problem in question. Measures of these responses range from numbers of devices or process installed or chemicals and labour utilized to the change in the number of visits to, or the degree of enjoyment at, a recreational beach.

Monetary values provide a common unit, or *numeraire*, by which otherwise incommensurate commodities or biophysical consequences and measures can be aggregated together. Monetary values also indicate the relative importance of specific consequences or commodities to individuals and, under certain conditions, to society as a whole. Estimation of relevant monetary values using market price data or other methodologies is the fourth key step in the procedure.

The economic implications of an environmental problem or phenomenon extend beyond the dollar values of the direct consequences and effects. First of all, to the extent that costs of inputs to a large number of enterprises (or government operations) and production processes are increased, the market prices of relevant goods and services may be increased to recover these costs. If specific market conditions do not permit price increases, those firms incurring the cost increases will suffer reduced profits. These economic consequences would be regarded as adverse by consumers who pay higher prices or the shareholders of firms which incur reduced profits.

On the other hand, the increased expenses incurred by firms or agencies become increased revenues to supplier firms or increased employment and wage payments if the higher costs involve added staff time. Economic resources are not lost but redirected within the economy as a result of the issue at hand. Some sectors and firms experience gains as the demand for their goods and services expands.

To the extent that recreational activities such as swimming or fishing are adversely affected, values derived from market prices generally understate the values that people actually ascribe to these activities.

The social implications of a particular environmental concern may well transcend measurable economic effects if stocks of particular resources are depleted so that some groups or communities lose their livelihood or if price changes affect different groups or localities unevenly.

Proliferation of zebra mussel colonies has resulted in two key adverse links with human activities. First, there is the potential for biofouling and clogging of water systems to cause serious damages and financial losses in municipal water treatment plants, industrial facilities and power plants if left untended. Second, accumulations of mussel shells on recreational beaches can reduce the attractiveness and utility of these resources to users.

Resources and effort must now be allocated to the removal of mussel infestations and to programs intended to prevent their accumulation in water systems. Moreover, authorities are searching for methods that could reduce zebra mussel populations in the Lakes, even before they begin infesting water intakes or other man-made structures. For each of these response actions, choices must be made as to the technologies or procedures to be applied and the level of effort to apply them. Comparisons of the costs of alternative response actions with each other and with the consequences of taking no action helps to make these choices.

First of all, the actual cases where zebra mussel damages, cleaning and removal or preventative actions have been taken in Ontario are documented.

Estimates of costs and the associated economic implications of the following responses to biofouling are examined in this paper:

- a. no removal of mussel colonies or preventative actions are taken. This is a worst case situation.

- b. mussels are removed and cleaned.
- c. preventative actions are taken or systems installed.
- d. monitoring and surveillance.
- e. research, technology development and technology transfer.

Separate estimates of biofouling effects are prepared for three potential geographical ranges of the zebra mussel throughout the Great Lakes: areas that are currently infested; the Great Lakes' shorelines of Ontario downstream from the infested areas; and all of the remaining shorelines of Ontario.

With regard to effects on beach use and enjoyment, estimates of the changes in beach visitation in areas that have recorded infestations of *Dreissena* are derived from a "beach use" model and data base prepared by Usher and Ellis (1987).

4. BIOLOGICAL CHARACTERISTICS, RANGE AND POTENTIAL EFFECTS

Dreissena polymorpha specimens were first identified in Lake St. Clair in June 1988. The animals found at that time were thought to be about 2 years old indicating that the original introduction probably took place during 1986 (Hart, July 1990). By May 1990, zebra mussels had been found at locations throughout the Great Lakes, from Cornwall on the St. Lawrence to Thunder Bay on Lake Superior. However, potentially troublesome colonies are so far found along Lake Erie shores, the Welland Canal and the Niagara River, Lake Ontario and Lake Michigan. Information on zebra mussel distribution throughout the Great Lakes is found in Griffiths, et al (1989).

A single female mussel can produce about 35,000 eggs each year during the summer and fall months when water temperatures rise above 12 degrees Celsius. The density of colonies or *druses* enhances successful fertilization and the production of thousands of free-swimming *veliger* larvae. The veligers can attach themselves to practically any horizontal surface where water flows are below 2.5 meters per second, including a docked ship. Ships with mussels and larvae attached have likely transported the animal to all parts of the Lakes.

Dreissena appears to have found virtually ideal environmental conditions in the lower Great Lakes and there are few natural predators of these organisms in North America. As a result, where mussel densities in Europe reach a maximum of 114,000 per square metre, colonies have been found to exceed 700,000 animals per square metre in Lake Erie (Griffiths et al., 1989). Adult mussels can survive anoxic conditions, exposure to air and extremely low water temperatures for many days, contributing further to the species' success in the Great Lakes.

Like all bivalve molluscs, *Dreissena* siphons water through its gills and removes microscopic phytoplankton as small as 0.7 microns in diameter. One adult zebra mussel filters about 1 litre of water each day and the filtering activity of thousands of mussels in a colony can noticeably increase the clarity of the surrounding water.

Dreissena's fecundity, mobility, small size and its propensity to colonize a wide range of substrates all contribute to its ability to cause biofouling in various types of water intake systems, presumably attracted by the flowing water that brings food within siphoning range. Europeans have contended with the zebra mussel for many decades. For example, as long ago as 1895, the Berlin water works were shut down because decaying mussels had contaminated the system (Griffiths et al., 1989).

In addition to clogging intake pipes and reducing water flows, the increased clarity brought about by zebra mussel filtering has resulted in increased algae and aquatic macrophytic growth near the Windsor water system intake. Decaying vegetation is apparently contributing offensive tastes and odours in the water that must be removed by costly carbon filtration.

Another concern related to biofouling, as yet unconfirmed, is the possibility that accelerated corrosion

to metals could occur under the anoxic conditions of a dense mussel druse (Spencer, 1990).

Where colonies form near recreational beaches, piles of mussel shells up to three feet deep have accumulated which reduce the attractiveness of the beach and present hazards to bare-footed bathers (London Free Press, August 14, 1990).

In addition to these two well-publicized adverse effects, researchers have postulated a number of other characteristics and consequences which may be associated with zebra mussels.

- a. the filtering actions of large colonies of mussels can increase the clarity of water. Increased clarity can be pleasing aesthetically but may have one or more of the following potential effects.
 - fish species that prefer turbid waters such as the walleyed pike (*Stizostedion vitreum vitreum*) will leave the area to seek more agreeable conditions.
 - phytoplankton, and the zooplankton that feed upon it, will be depleted by zebra mussels leaving little for fish and other aquatic organisms. The long-term consequences for Great Lakes' fisheries populations are uncertain at this time.
 - increased water clarity and light penetration allows the growth of benthic algae and aquatic plants. These plants can cause taste and odour problems in municipal water systems.
 - zebra mussels could be employed to remove excess nutrients and pesticides from natural waters. Press reports have claimed that the Russians are experimenting with *Dreissena* for such purposes (North Bay Nugget, June 15, 1990).
- b. colonizing rocky areas that fish use for spawning may smother the fish eggs and crowd out spawning fish. On the other hand, smaller clusters of mussels can help to protect the fish eggs laid among them. The net effect is not yet determined.
- c. while many freshwater molluscs serve as intermediate hosts of parasites in humans, *Dreissena polymorpha* has not been found to be heavily infected with such parasites. Continued surveillance is recommended to determine whether *Dreissena* becomes a vector for such parasites (O'Neill, 1989).
- d. zebra mussels may also be used in biomonitoring studies because the organisms absorb contaminants which may then be analyzed (Alekseyer and Antipin, 1986 as quoted in Mackie et al., July 1989).
- e. zebra mussels may be a source of new pharmaceutical products and they have been used as calcium supplements in livestock feed in Europe.

The areas of Great Lakes shoreline that are most infested at this time extend from Windsor on the Detroit River through all of Lake Erie and include the Niagara River and Welland Canals. The Lake Ontario shoreline and the St. Lawrence River are currently at most risk of future problematic mussel infestations in Ontario. The St. Clair river and Lake Huron shoreline up to Kincardine is also currently viewed as at risk from colonizations that could cause biofouling or beach littering. The remaining Great Lakes shorelines and urban settlements on both sides of the border are at somewhat lower risk although those harbours with substantial shipping traffic would face proportionately higher risks of mussel infestation.

Authorities also fear invasions of inland waterways where thousands of home and cottage water systems could be at risk. This issue is, however, beyond the scope of the present investigation.

5. CURRENT DAMAGES, CONTROL MEASURES AND RESPONSES

There are, to date, at least 14 biofouling cases in Ontario where zebra mussel infestations have

caused damages or have required expenditures for repair or removal. These cases include three industrial plants, one thermal power plant and 10 municipal water treatment systems. The consequences of biofouling at these plants range from reduced water flows and pressures, abandonment of intake pipes, temporary shutdowns and the installation of chlorination facilities to kill the organism prior to removal. Each of these cases are summarized in Table 1. The locations of these occurrences are also shown in Table 1.

Left unattended, mussel infestations can disable fire protection systems in power plants and industrial facilities. Of particular concern to power utilities is the lodging of mussels in small diameter pipes leading to over-heating of cooling condensers and major damage to the generating facility. Reduced flows in an industrial plant can result in reduced production, higher unit production costs and reduced profitability.

Shutdowns of an industrial plant such as a refinery can involve expenses of more than \$750,000, not counting lost production and revenues (Atwell, 1990). So far, Ontario establishments have been spared such extreme consequences.

Municipal water treatment plants that experience reduced flows because of mussel blockages suffer increased operating costs (i.e. increased \$ per unit of water pumped) and reduced energy productivity. A municipal water treatment plant at Monroe, Michigan, one of the first establishments in all of the Great Lakes to experience zebra mussel intrusions, had to install a temporary intake system while mussel encrusted components were cleaned or replaced. The city of Monroe spent over \$6.3 million on cleaning, repairs and the temporary pumping facilities (Lepage et al., November 1989). The water intake structures and pipes at West Lorne and Tilbury, Ontario had to be abandoned because of infestations and new installations are under construction at a cost of about \$5-6 million for the two projects.

To date, capital and other one-time expenditures directly attributable to zebra mussel biofouling in Ontario amount to about \$8.7 million as shown in Table 1. Compared with the relevant budgets and expenditures normally associated with Ontario Hydro, industrial plants and municipal water and sewage utilities, these expenses are as yet relatively modest. However, they may be a portent much greater financial requirements in the future.

Once in place, removal of colonies from intake structures and pipes is a daunting and arduous task. Moreover, experience and technologies available in North America are as yet limited. A variety of methods and technologies are being investigated either to remove zebra mussels already ensconced in a water intake system or to prevent their establishment in the first place.

Methods for the removal of *Dreissena polymorpha* colonies currently in use include hand scraping by divers, "hydro blasting" with high pressure hoses, pulling mechanical scraping devices called "pigs" through an intake pipeline, killing mussels prior to removal with hot water or chemicals such as chlorine and abandonment and replacement of clogged pipes. Factors that impede these efforts and raise the costs of their implementation include weak pipes that cannot withstand the stresses of mussel removal, limited access to pipes by divers and cleaning equipment, the need to shut down plants to effect removal and repairs and the ability of the adult mussel to withstand extreme temperatures and biocides such as chlorine if the procedures are not applied properly. Hand scraping, pipeline cleaning contractors and chlorination were employed at the three industrial plants noted in Table 1.

In Europe where *Dreissena* has been endemic for many decades, intake structures and pipes have been "twinning" to permit uninterrupted operation while one pipe is being cleaned. Intake pipes are also designed to facilitate cleaning and mussel removal.

Other, somewhat esoteric, mussel removal methods of unknown efficacy have been reported recently including electric shock and acoustic (sound) devices to shatter the animal (Davidson, August 9, 1990).

A variety of chemical biocides in addition to chlorine are being tried out to help remove infestations and prevent their formation. Potassium permanganate, oleanolic acid glucoside (an active ingredient in the African soapberry), bromine, copper sulphate, cyanuric acid, ammonium nitrate and ozone are all under investigation. So far, chlorine has proven to be the most cost-effective material available.

For the hundreds of Great Lakes water-using establishments not yet encrusted with zebra mussels,

TABLE 1 CURRENT INFESTATION OF ZEBRA MUSSELS IN ONTARIO AND THEIR EFFECTS

PLANT/LOCATION	INFESTATION EFFECTS	RESPONSES	POTENTIAL EXPENDITURES	SOURCE
Ford Engine Plant, Windsor, Detroit River.	- Mussels found in cooling and service systems and intake pipe. - Clogging and reduced flows in pipes < 4".	Temporary chlorination	About \$3,000 for one week	Personal interview, Aug. 31, '90
General Motors, Parts Plant, St. Catharines, Lake Ontario.	- Mussels in fire reservoir, intake strainer, service system	Chlorination, 2 weeks Follow-up 1990.	May - \$130,000 for 2 weeks. Sept. - \$95,000 for 2 weeks.	Fred Konkle, GM, Personal communication, Aug. 1990.
H. J. Heinz, food processing plant, Leamington, Lake Erie.	- Intake pipe clogged.	Mechanical cleaning and scraping.	Not available	Canada Pipeline Cleaning Ltd. Personal comm.
Ontario Hydro, Naticoke Thermal Generating Station, Lake Erie.	Mild infestation of service water system, small clogged.	Some mechanical scraping and removal; chlorination system extended.	Extension of chlorination system - \$300,000; Bioboxes \$8,000; Technicians at Naticoke - \$38,400/yr. Cleaning part of annual maintenance. Corporate salaries \$672,000 per year.	Ontario Hydro
Tilbury Water Treatment Plant, Lake Erie	Mussels in intake pipe; reduced flow capacity by 45%.	Replacement of intake pipe; extension of chlorination.	\$2,126,000	Ministry of the Environment.
West Lorne Water Treatment Plant	Mussels in intake pipe; reduced flow capacity.	Extension of chlorination system; replacement of intake pipe and low lift system.	\$4,380,000	Ministry of the Environment
Amherstburg Water Treatment Plant	Reduced flow capacity.	Extension of chlorination.	\$45,000	Lafontaine <i>et al.</i> (1990)
Blenheim Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	\$100,000	Lafontaine <i>et al.</i> (1990)
Kent County Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	\$65,000	Lafontaine <i>et al.</i> (1990)
Harrow-Colchester Water Plant	Reduced flow capacity.	Extension of chlorination system.	\$45,000	Lafontaine <i>et al.</i> (1990).
Elgin Water Treat. Plant	Reduced flow capacity.	Extension of chlorination system.	\$137,000	Lafontaine <i>et al.</i> (1990).
Belle River Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	\$130,000	Lafontaine <i>et al.</i> (1990).
Tecumseh Water Treatment Plant	Reduced flow capacity.	Extension of chlorination system.	\$45,000	Lafontaine <i>et al.</i> (1990).
Mitchell's Bay Plant	Reduced flow capacity.	Extension of chlorination system.	\$32,000	Lafontaine <i>et al.</i> (1990).

methods of prevention are of particular interest. Placement of intake pipes in deeper water, burying intake pipes and structures where feasible, specially designed intake structures with screening and devices to continuously clean screens, maintenance of water flows above 2.5 metres per second, anti-fouling coatings on exposed surfaces and treatment with chlorine, ozone or other approved biocides periodically to kill larvae and juvenile animals in the system are all under trial and investigation.

Where facility configurations permit, periodic flushing with hot water (above 40 °C) has been found to be effective. This approach is currently employed at a small thermal electric power plant operated by the Welland Canal Authority (Aquatic Sciences, 1990). So far, the major water-using installations in Ontario, such as Ontario Hydro and municipal water treatment plants, are installing systems to chlorinate their intake water during 6 months of the year to kill veliger larvae that get into the systems. Such facilities consist of a tube or pipe to carry the chlorine to the lake end of the intake pipe as well as chlorination pumps, meters and storage tanks.

Although chlorine is widely used as an oxidizing agent in industry and a disinfectant for sewage treatment and water treatment plants, its use in zebra mussel control defines it as a pesticide and requires that a license from the Ministry of the Environment be obtained for this application.

An integral part of a program of prevention is monitoring using "bio-boxes" to determine the presence of veligers and the effectiveness of controls and inspections by divers and remote TV cameras. In addition, research on a variety of removal and preventative measures are being carried out primarily by government and some larger industrial firms such as Ontario Hydro.

Another form of "control" involves identifying and encouraging natural predators of *Dreissena* in North America. This approach would help control the beds of mussels that contribute to beach infestations and accumulations. Certain species of diving ducks consume zebra mussels and appear to be increasing their populations around infested localities. One species of indigenous North American fish, the American drum, also eats zebra mussels but is itself of little interest to recreational and commercial anglers.

Finally, relevant government authorities are reviewing legislation and regulatory requirements for the treatment and disposal of ballast water from foreign ships. While it is too late for the zebra mussel, tighter controls could prevent the unintended immigration of new undesirable species.

6. POTENTIAL COSTS OF RESPONSES TO BIOFOULING

If the *Dreissena* invasion continues unchecked, many more direct water-using facilities will be at risk from biofouling. In order to avoid the potentially serious damages that are possible, these establishments must choose whether to install preventative measures or to implement a periodic cleaning and removal program that is frequent enough to ensure that druses do not become established. Systematic monitoring involving at least two visual inspections by divers each year and the installation of devices such as "bio-boxes" to detect veligers would help to determine when removal or chemical control measures must be applied.

Preliminary estimates of the costs of a monitoring program and of installing or modifying chlorination systems at 8 Ontario Hydro power plants, 86 municipal water treatment plants and 67 industrial plants that are located on the Great Lakes and are at risk from zebra mussel infestations have been developed. The estimates, which are summarized in Table 2, are disaggregated by three geographical areas:

Area A Currently infested shoreline between Windsor and Niagara-on-the-Lake.

Area B Shorelines at Risk from Kincardine to Windsor and Niagara-on-the-Lake to Cornwall.

Area C Rest of the Great Lakes.

Other types of control systems may be applied in these plants, such as ozonation, but alternative systems are likely to be much more costly and, as noted, chlorination is currently the system of choice among those agencies most directly involved.

Ontario Hydro thermal and nuclear generating stations already have chlorination systems in place and the capital cost estimates involve modifying the chlorination systems to introduce the chlorine at the intake structure out in the lake. An amount of extra chlorine will likely be required after these modifications are made but could not be estimated at this time. Since few if any of the industrial plants have chlorination systems in place, all of the chlorine used will be incremental. The costs of chlorine shown in Table 2 that may be used by industrial plants are based on a dosage of 5 ppm.

Costs of cleaning and removal could be estimated only for Ontario Hydro facilities, based on reported zebra mussel removal costs incurred at the Detroit Edison thermal power plant at Monroe, Michigan (Kovalak *et al.*, 1990). Estimates for intake pipe cleaning and removal at municipal water treatment plants and industrial facilities could not be generated at this time.

Estimates of potential expenditures for monitoring activities are presented for each of the three types of water-using plants as well.

Estimation procedures, algorithms and the input information used to prepare the figures shown in Table 2 are detailed in Donnan and MacKay (forthcoming).

It is clear from Table 2 that municipalities will likely have to incur the majority of these potential retrofitting expenditures or about \$148 million out of \$165 million in total expenses for all "Zones." These estimates are also over and above the expenses listed in Table 1.

If the systems installed for prevention are successful, little if any removal and cleaning costs will have to be incurred at municipal and industrial plants. Expenditures for chlorine and monitoring may be underestimated because increased demand for chlorine chemicals and monitoring services (ie diving) could push up prices over the next several years. Estimates of monitoring for each sector are probably underestimated in any event.

Not included in these estimates are \$3.5 million in research projects committed by Ontario Hydro over the next 3 years and an unknown amount to be spent on zebra mussel research by the provincial government during the foreseeable future (Spencer, February 1990).

One-time expenses of \$165 million and annual expenditures of about \$10 or \$11 million per year, while not insubstantial, are not large in comparison to other expenditure categories incurred by the affected establishments. On the other hand, there are many uncertainties associated with these estimates which could result in upward revisions.

It does not appear that the zebra mussel will impose intolerable financial burdens on Great Lakes water users during the near future. Moreover, the estimates presented here represent opportunities to the firms and agencies which offer goods and services in response to zebra mussel incursions.

A very tentative conclusion is that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. One of the best investments that can be made at this time would be increased monitoring and surveillance by all parties at risk.

7. IMPLICATIONS FOR RECREATIONAL BEACHES

At least 10 Lake Erie beaches in the southwest part of Ontario have experienced nuisance levels of littering by zebra mussel shells. Using a Beach-Use model developed by Usher, Ellis and Michalski (1987), the implications of reduced aesthetics and attractiveness of beaches in terms of reduced visitation and use rates has been explored.

The model includes an "attractiveness index" which may be used to classify a particular beach as "excellent", "very good", "acceptable", "marginal" and "unsatisfactory". Ten Lake Erie beaches in Essex, Kent and Elgin Counties that are included in the model have recorded accumulations of zebra mussel shells. The "attractiveness index" for these beaches were reset to "marginal" and "unsatisfactory" and the resulting shifts

in beach attendance or visitation were estimated with the model.

If the zebra mussel becomes more widespread, it may affect beaches over a much wider range of the Great Lakes. In this analysis, it was postulated that all beaches could be adversely affected by *Dreissena* from Kincardine (on Lake Huron) to Cornwall, Ontario, on the St. Lawrence River at the Ontario-Quebec border. The "attractiveness index" was reset to "marginal" and "unsatisfactory" for these beaches and the model run for each scenario.

The results of these analyses are shown in Table 3. In the 10 beaches currently infested with zebra mussels, beach use occasions could be reduced by as much as 18% if the effects caused by zebra mussels only partially reduced the attractiveness of the locations. However, if the adverse effects are perceived by people to be of major importance, beach attendance would be reduced by as much as 50%.

The model assumes that people would go to other beaches in Southwestern Ontario which are located on inland waters or on Lake Huron and the Georgian Bay. Expenditures associated with these beach occasions (ie travel, food, accommodation, etc.) would not likely leave the province under either level of perceived attractiveness because the total number of beach use occasions in Ontario are assumed to stay constant.

Real losses in utility and enjoyment may be experienced by beach users who continue to visit mussel infested locations or those who go to other locations which then become more congested.

Where it is assumed that all beaches between Kincardine on Lake Huron and Cornwall on the St. Lawrence River experience reduced attractiveness (to "marginal"), the number of visits to these beaches falls by about 12.5%. Under these conditions, people would likely shift their visitation north to the Georgian Bay, to inland lakes in Eastern Ontario, the Southwest and around the "Golden Horseshoe".

There are, as yet, no clear means of preventing the spread of *Dreissena* along shorelines and further deterioration of beach quality by mussel shells could have severe local economic effects but research is needed to monitor and enumerate these consequences.

8. OTHER BIOLOGICAL INVASIONS OF THE GREAT LAKES

At least 38 species of fish have been introduced into the Great Lakes since 1819, either deliberately or intentionally (Emery, 1985). Ten of these "exotic" species are recognized as having major influences on aquatic ecosystems in the Great Lakes and their uses by people. Four of these earlier "invaders", the sea lamprey (*Petromyzon marinus*), the alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*) and the white perch (*Morone americana*) have had particularly adverse effects.

Lamprey eels were present in Lake Ontario since the early 1980's but only gained access to the upper Lakes through the Welland Canal in 1921 (Christie, 1974). However, unlike the zebra mussel, it took another 20 years for this invader to encroach upon the affairs of man. The other exotic species were introduced before or just after the turn of the century. Major effects and consequences were not realized until the 1940's and 1950's.

The consequences of concern were the decline of important indigenous species in the Great Lakes, including the lake herring (*Coregonus artedii*), certain varieties of walleye and the lake trout (*Salvelinus namaycush*), as a result of predation, competition and external habitat destruction.

The predatory activities of the sea lamprey have been particularly damaging to the highly valued lake trout (*Salvelinus namaycush*), whitefish (*Coregonus sp.*) and burbot (*Lota lota*) populations native to the open waters of the Great Lakes. By 1949, Lake trout populations and commercial catches in Lakes Huron and Ontario collapsed and by the early '60s, the lake trout fishery in Lake Superior was wiped out (Christie, 1974). Similarly, lake whitefish (*Coregonus clupeaformis*) suffered lamprey predation when trout and burbot were no longer available. Commercial catches of whitefish were virtually eliminated in Lakes Michigan and Huron by 1954 and drastically reduced in Lakes Superior and Ontario by the early 1959's due in great part to lamprey predation (Christie, 1974).

TABLE 2: SUMMARY OF COST ESTIMATES FOR THE CONTROL OF ZEBRA MUSSELS IN ONTARIO
(MILLIONS OF \$)

ONTARIO HYDRO POWER PLANTS: 8 PLANTS				
	CAPITAL	PREVENTION O3A/CHLORINE	REMOVAL & CLEANING	MONITORING
ZONE A (1)		0.50	0.58	
ZONE B (2)		0.90	0.62	
ZONE C (3)		0.40	0.25	
TOTAL:	1.80	N/A	1.25	0.72
MUNICIPAL FACILITIES: 86 PLANTS				
	CAPITAL	PREVENTION O3A/CHLORINE	REMOVAL & CLEANING	MONITORING
ZONE A	30.50			
ZONE B	92.90			
ZONE C	25.30			
TOTAL:	148.50	N/A	N/A	0.86 (4)
INDUSTRIAL PLANTS: 67 PLANTS				
	CAPITAL	PREVENTION O3A/CHLORINE	REMOVAL & CLEANING	MONITORING
ZONE A	5.00	5.20		
ZONE B	8.30	2.30		
ZONE C	1.10	0.08		
TOTALS:	14.40	7.58	N/A	0.67 (4)
TOTALS:				
ZONE A -	35.80	5.20	0.58	
ZONE B -	102.10	2.30	0.62	
ZONE C -	26.80	0.08	0.25	
GRAND TOTAL:	164.7	7.58	1.25	2.25

NOTES:

- (1) ZONE A: CURRENT INFESTED ZONE - WINDSOR TO NIAGARA
 (2) ZONE B: SHORELINES AT RISK - KINCARDINE TO WINDSOR
 AND NIAGARA-ON-THE-LAKE TO CORNWALL
 (3) ZONE C: REST OF GREAT LAKES
 (4) MONITORING FOR MUNICIPAL AND INDUSTRIAL FACILITIES CONSISTS OF
 DIVES TOTALLING \$5,000 FOR 2 DIVES PER YEAR, AND \$5,000
 FOR OPERATING AND CAPITAL COSTS OF BID-BONES

TABLE 3: POTENTIAL CHANGES IN DAILY VISITS TO BEACHES
RESULTING FROM REDUCED ATTRACTIVENESS (000's of occasions)

	ATTRACTIVENESS INDEX RATING					
	MARGINAL			UNSATISFACTORY		
	ORIGINAL USE	NEW USE	% CHANGE	ORIGINAL USE	NEW USE	% CHANGE
10 BEACHES CURRENTLY INFESTED WITH DRISSENA	1,542	1,266	-17.90%	1,542	822	-46.69%
ALL BEACHES BETWEEN KINCARDINE AND CORNWALL	10,013	8,718	-12.93%	N/A	N/A	N/A

After the collapses of populations of predatory fish species, smelt stocks increased rapidly in Lakes Ontario and Superior, alewife populations burgeoned in Lakes Superior, Huron and Michigan, cisco (*Coregonus johanna*) stocks expanded, at least briefly, in all the Lakes and the indigenous lake herring (*Coregonus artedii*) stocks collapsed throughout the region. Researchers believe that lamprey predation together with overfishing are the primary causes of these major aquatic population disturbances (Christie, 1974).

The measured effects of these exotic species have all occurred during the past 40 years and the population dynamics of aquatic populations in the Lakes have yet to be stabilized. The primary linkages to man in each case are reductions in commercial catches of indigenous species. Substantial recreational utility has undoubtedly been lost as a result of population collapses of various highly prized game fish. However, monetary values associated with efforts to control the invader and with the profit and enjoyment (utility) of restoring desired fish species that result of this control has been enumerated only for the lamprey eel.

In 1955, the Great Lakes Fishery Commission (GLFC) was formed by treaty between the U.S. and Canada to promote and coordinate efforts to control the sea lamprey and restore lake trout populations in the Great Lakes. Commission sponsored research eventually led to the development of 3-trifluoromethyl-4-nitrophenol (TFM), a selective toxicant which has been used since the early 1960's to kill the ammocoetes larvae of the lamprey in nursery streams (Applegate et al., 1961).

These control efforts have led to a partial recovery of lake trout and whitefish populations in many areas of the Great Lakes. Lamprey control, together with salmonid stocking programs in the Great Lakes are the primary fisheries management activities carried out by federal, State and provincial (Ontario) governments on the Great Lakes. Sport and commercial fishing interests are the primary beneficiaries of these programs. Sport fishing for introduced salmonids, lake trout, walleyes, whitefish and other species has come to dominate commercial fishing on the Great Lakes in terms of direct expenditure, associated employment and political attention. (Talhelm, 1987; Spaulding and McPhee, Nov. 28, 1989).

Since its inception in 1955, the Great Lakes Fishery Commission has spent several millions of dollars each year on sea lamprey control. In 1988, the Commission spent \$6.2 million (Canadian) on the sea lamprey control program, \$1.2 million on research and barrier dams and \$ 0.6 million on administration or about \$8 million in total (Spaulding and McPhee, Nov. 1989). The funds originate from the U.S. and Canadian governments.

As part of an evaluation of the Commission, Spaulding and McPhee (Nov. 1989) estimated the monetary values associated with recreational fishing that would be reduced if the sea lamprey control program were to be terminated in the Great Lakes. Increased lamprey predation on salmonids would substantially reduce the fish available for harvesting by recreational fishermen. Salmonid fishing days would be lost as the result of three behavioural responses: 1) some anglers that fish for salmonids will no longer fish in the Great Lakes; 2) some salmonid anglers will switch to non-salmonid species, and 3) increased angling effort on non-salmonids will cause some non-salmonid anglers to abandon the Great Lakes as well.

The total net value of these consequences was estimated at \$318 million (Canadian) per year (Spaulding and McPhee, Nov. 1989). Because salmonid fish only account for about 3% of the 1988 Canadian landed value, lamprey control would have little effect on that sector. The authors note that these consequences should also be attributed in part to salmonid stocking programs which cost a total of \$10.2 million (Canadian) in 1988 (Spaulding and McPhee, Nov. 1989).

Therefore, while sea lamprey control costs about \$8 million (Canadian) each year, the recreational utility that could be lost if the control measures were eliminated would amount to over \$300 million per year. This latter value would be comparable to the values associated with the damages that *Dreissena* could cause if no defensive expenditures or control measures were incurred.

9. CONCLUSIONS

To date, capital and other one-time expenditures directly attributable to 14 documented zebra mussel

biofouling cases in Ontario amount to about \$8.7 million.

Ontario municipalities around the Great Lakes will likely have to incur the majority of potential expenditures for zebra mussel prevention and control or about \$148 million out of total \$165 million. Compared with the relevant budgets and expenditures normally associated with Ontario Hydro, industrial plants and municipal water and sewage utilities, the expenses that have been incurred to date and that have been forecast are as yet relatively modest. However, they may well be a portent much greater financial requirements in the future.

A very tentative conclusion is that the consequences of the zebra mussel infestations and the costs incurred to respond to them will not cause undue economic or social repercussions so long as Great Lakes water users are vigilant and implement control or preventive measures in time. One of the best investments that can be made at this time would be increased monitoring and surveillance by all parties at risk.

There are, as yet, no clear means of preventing the spread of *Dreissena* along shorelines and beaches. Further deterioration of beach quality by mussel shells could have severe local economic effects but research is needed to monitor and enumerate these consequences.

The zebra mussel is the most recent of many biological invasions of the Great Lakes over the past century. Hopefully, it will be the last.

REFERENCES

- Applegate, V.C., Howell, J.H., Moffett, J.W., Johnson, B.G.H. and Smith, M.A. Use of 3-trifluoromethyl-4-nitrophenol as a selective sea lamprey larvicide. Great Lakes Fishery Commission Technical Report No. 1, 1961.
- Aquatic Sciences Inc., The Zebra Mussel: An Investigation of Present Distribution and Potential Impact in the Welland Canal System and Associated Structures, May 24, 1990.
- Aquatic Sciences Inc., Zebra Mussel Control Program Experimental Service Water Chlorination : General Motors of Canada Ltd.
- Aquatic Sciences Inc., Zebra Mussel Control Program Experimental Service Water Chlorination Phase I: Ford Motor Company of Canada Ltd.
- Atwell, D., Personal Communication, October 1990.
- Christie, W.J. "Changes in the Fish Species Composition of the Great Lakes". Journal Fisheries Research Board of Canada. Vol.31, No.5, 1974, pp. 827-854.
- Davison, J., "Tests Could be Music to Mussel Fighters' Ears", The Standard, August 9, 1990.
- Emery, L. Review of Fish Species Introduced into the Great Lakes, 1819-1974. Great Lakes Fishery Commission Technical Report No. 45, 1985.
- Fisheries and Oceans Canada. "Contaminant Effects on Great Lakes Aquatic Biota with Emphasis on Fish", Draft., undated.
- Geigen-Miller, Peter, "Invasion of the Zebra Mussels", London Free Press, October 6, 1990.
- Griffiths, R.W., Kovalak, W.P., and Schloesser, D.W., The Zebra Mussel, Dreissena Polymorpha (Pallas, 1771), in North America: Impact on Raw Water Users, December, 1989.
- Hart, M., "Invasion of the Zebra Mussels", Atlantic Monthly, July, 1990.
- Kovalak, William P., Longton, Gary D. and Smithee, Richard D. "Infestation of Monroe Power Plant by the zebra mussel (*Dreissena polymorpha*)", from Zebra Mussels: The Great Lakes Experience, A Conference at the University of Guelph, Guelph, Ontario, Feb. 1990.
- La Fontaine, Cowie, Buratto and Associates, Ltd. (Draft) "Zebra Mussel Control Measures - Preliminary Report, 1990.
- LePage, W.L., The Impact of Dreissena Polymorpha on Water Works Operations at Monroe, Michigan (USA), November, 1989.
- Leach, Joe, Distribution of Zebra Mussels (as of May 29, 1990).
- MacArthur, M., "Shellfish's Spread Along Shoreline Termed Inevitable", London Free Press, August 14, 1990.
- Mackie, G.L., Gibbons, W.N., Muncaster, B.W., and Gray, I.M., The Zebra Mussel, Dreissena Polymorpha: A Synthesis of European Experiences and A Preview for North America, April, 1990.
- North Bay Nugget, "Hated Zebra Mussel May be Victim of Ignorance", North Bay Nugget, June 15, 1990.
- O'Neill, C.R. Jr. and MacNeill, D.B., Dreissena Polymorpha, An Unwelcome New Great Lakes Invader.

Factsheet, New York State Sea Grant Co-operation Extension, November, 1989.

Spaulding, W.M and McPhee, R.J. "The Report of the Evaluation of the Great Lakes Fishery Commission by the Bi-National Evaluation Team. Vol.2, An Analysis of the Economic Contribution of the Great Lakes Sea Lamprey Program." Nov. 28, 1989.

Spencer, F.S., Zebra Mussel Research Program: Ontario Hydro Research Division, February 16, 1990.

Stanley, J. , Economic Impact of the Zebra Mussel on the Great Lakes, circa 1990.

Stoffle, Richard W., Rasch, Danny L. and Jensen, Florence V. "Urban Sports Anglers and Lake Michigan Fishery Policies." Coastal Zone Management Journal, Vol. 10, No. 4., 1983, pp. 407-427.

Talhelm, Daniel R., "Economics of Great Lakes Fisheries: a 1985 Assessment." in Special Economic Report, Great Lakes Fishery Commission, 1987.

Toronto Star, "Bruce Plant to Kill Zebra Mussels", Toronto Star, August 9, 1990.

Usher, A. and Ellis, J., Beach-Use and Environmental Quality in Ontario, Ontario Ministry of Environment, Policy and Planning Branch, May, 1987.

Wells, L. and McLain, a. Lake Michigan: Man's Effects on Native Fish Stocks and Other Biota. Great Lakes Fishery Commission Technical Report No. 20, 1973.

ECONOMICS AND TECHNICAL CHANGE: THE WATER RESOURCE CONUNDRUM.
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ABSTRACT

One of the most potent, but least understood, functions of a market system of economic organization is its ability to motivate technological change. The market system provides incentives for private gain, which, in turn, leads to the generation of new technologies. The key to this process lies in the ability of prices to reflect accurately the value of the resources devoted to respective economic activities.

A major problem of environmental management arises because environmental resources are, almost without exception, undervalued in relation to their contribution to economic activities. This paper uses the case of municipal and industrial water pricing to document the almost-negligible cost of water resources in relation to the costs of other goods and services, and to production costs. The data are based upon recent surveys of municipal and industrial water prices. These survey indicate municipal water prices in Ontario (including sewer charges) averaging less than \$0.60 per cubic meter, and industrial charges which are substantially below 1% of production costs.

The paper concludes by discussing the implications of the current state of water pricing for technological change in the water industry, and with suggestions for improvement. The overall thesis is that until water prices reflect better the value of the resource to society, incentives for technological change will continue to be significant retarded.

¹The opinions expressed in the paper are those of the authors, and not necessarily those of Environment Canada

1. INTRODUCTION

Since the 1960s, interest in the environment and its problems have grown at an ever-increasing rate. To-day, environmental issues, ranging from pollution to export, are usually listed among the top three issues in public opinion polls. We do not have to think very long to find the reasons for this "popularity".

Water pollution problems raise concerns in many parts in many areas of the country, notably the Great Lakes and major estuarine areas. Although water management has taken significant strides in overcoming certain pollution problems, significant ones remain, such as toxic substances. Water shortages are common in many areas, most importantly in the Western Interior, but even in southern Ontario, a peninsula built into the heart of the world's largest freshwater body. Canadians have slowly realized that 9% of the world's annual renewable water supply is not, by itself, a guarantee of freedom from water shortage. Resource distribution and pollution have fixed that perception. Capital shortages for water projects are so severe that the infrastructure of major urban areas is deteriorating rapidly.

Each of these problems has technological dimensions. Some are obvious, such as the need to upgrade and improve conveyance and treatment methods. Others are not, and this paper addresses one of those - namely, the mechanisms which underlie technological developments, and which allow the advancement of living standards in many societies throughout the world, but which seem to have been blunted in their effects on the use of environmental resources such as water. It is clear that technical developments do not just "happen", or fall from the sky. On the contrary, there are very clear reasons why change occurs, and, indeed, why it occurs in some areas and not in others. In water management, the mechanisms underlying technological change are not well understood, and have rarely even been acknowledged. We believe, however, that they lie at the heart of any hopes for significant improvements in environmental management.

2. ECONOMICS AND TECHNICAL CHANGE

Schmookler (1966) defined technology as "the social pool of industrial arts." Clearly, technological change is an change in this pool. The central issue is what causes these changes, in other words what conditions have to be present for advancement to occur. This question has concerned many generations of economists and social scientists, and it is to a brief explanation of their findings that we now want to turn.

The concern of people over resource scarcity reaches back in history at least into the eighteenth century. Well before Thomas Malthus explained how unrestrained population growth would be held in check and in misery by the limited amount of food producing

land, the Physiocrats of eighteenth century France and the great Adam Smith reasoned that all wealth ultimately came from the land and so the limits of land would limit production. This concern over physical limits to productivity has proven less than accurate for many areas of the world, at least into the latter part of the twentieth century. As Charles Schultze stated:

"Living standards in modern Western countries are, by an order of magnitude, superior to those of the early 17th century. Had the triumph of the market meant only a more efficient use of technology and resources then available, the gains in living standards would have been minuscule by comparison. What made the difference was the stimulation and harnessing of new technologies and resources."

This statement supports strongly the findings of Nobel prize winner Robert Solow, who demonstrated that over 85% of technological advancement in the U.S. economy during a forty year period was due to the operation of economic forces through the medium of the marketplace (Solow, 1955).

The conclusion of importance here is that economic forces are largely responsible for incentives which lead to technological change. On the supply side, the progression of technology has vastly increased the resources available, through discovery of new reserves and stocks of everything from petroleum to fish. Supplies have been expanded even more by advances enabling the use of less accessible resources, of lower quality, and lesser concentrations. Even land, though limited in the spatial sense, has been augmented enormously in its capacity to produce crops (Pearse and Tate, 1990).

On the demand side, technology has progressively reduced and eliminated our dependence on particular resources for particular resources for particular purposes, broadening the range of materials available to producers, and improving the suitability among them. Timber is no longer needed to construct buildings and ships because there are now a dozen new materials to choose from. Societies no longer need copper to transmit energy and messages because materials like aluminum and fibre optics, made of much more ubiquitous raw material, will do the same job. Indeed, we no longer need any materials for these purposes, because electronic signals can be transmitted without them. All this innovation has more than offset the depletion of resources through consumption. Notwithstanding the enormous economic growth of the

¹Military need constitutes one of the other primary technological change stimulants, but this need has proven of less importance than economic incentive.

past century, the demand for almost all natural resource commodities and food has risen slower than the supply. The result is that the real price of natural resource products -- that is, the cost relative to manufactured goods, or to all goods and services taken together -- has gradually declined (Pearse and Tate, 1990).

These findings, which are readily acknowledged by most resource specialists, lead to a cruel paradox environmentally. On the one hand, technology has led to the creation, in Western societies, of enormous gains in living standards for all groups in society, although, undoubtedly, not all have benefited equally. On the other, the same technology and productivity has caused substantial, and in some cases catastrophic, environmental degradation. Thus, why, for example, should economists advocate the use of economic instruments to help solve environmental problems when economic forces have done so much harm?

If various sectors of the economy are examined carefully with respect to their uses of environmental resources, we quickly find that economic forces, such as the interplay of supply and demand to determine realistic prices, have been almost totally absent. Thus, it is no surprise that technologies are extremely traditional, resources are overused, wasted and, in some cases, destroyed. It is almost as if society has ignored one of its strongest forces, namely economic incentive, and then attempted to do an effective job of coping with environmental management (Tate, 1984). The sooner that economic forces are recognized as being of central importance in promoting technological change in the water industry, the quicker and more effectively will water managers be able to do their jobs.

3. TECHNOLOGY AND WATER RESOURCES

What is meant by traditional technology? Certainly, the water resource trade journals, on the surface, seem to suggest that water technologies have developed substantially. The Science Council of Canada even suggests that an export industry should be built of Canadian technology.

Examples of the persistence of traditional technologies are easy to identify. The following examples are illustrative, although by no means exhaustive. First, Environment Canada's industrial water use surveys have demonstrated that the percentage of industrial water deriving from recirculation has fallen over the 1972-1986 period (Table 1). The concept of a use rate is a simple way of looking at this. If gross water use, or the total amount of water used in producing a product is divided by total water intake, and multiplied by 100%, the result is a use rate. The higher the rate, the higher the level of recirculation. In almost all cases, the use rate fell, showing that recirculation rates declined during this 14-year time span.

Second, the average Canadian per capita water use from municipal systems is 350 litres per day, second only to that of the U.S., and over double that of many European countries. Also, of the water pumped in many Canadian municipalities, less than 75% can

Table 1 Use rate (%) for Canada and Ontario, 1972 - 1986

Year	Canada		Ontario	
	Total	Manufacturing	Total	Manufacturing
1972	172	233	148	208
1981	152	208	120	185
1986	142	198	114	188

Note: The "total" industry columns include mineral extraction, manufacturing and thermal power generation sectors. The use rate equals (total gross use/total intake) x 100%.

be accounted for by deliveries to customers. Third, water use inside the home is excessive. The typical toilet uses 20 litres per flush, and showers use over double the amount of water required for effectiveness. Postel (1985) showed that a typical North American home could save over \$100 per year in energy costs alone by using water efficient showerheads. Fourth, recent research done at McMaster University (Patry and Takacs, 1990) showed that waste treatment plants are less efficient the greater the amount of water pumped through them. Fifth, irrigation in Western Canada supports the growth of crops that could probably be grown more cheaply in more humid areas. Irrigation causes enormous amounts of water consumption in an area where there exist much more highly valued water uses. Finally, in all parts of Canada, we afford industries free access to waterways for waste deposition. Serious water pollution problems have resulted.

Improvements are certainly possible. Research in water use by industry (Kollar and MacAuley, 1980) showed that water can be recycled up to nine times through advanced industrial plants. In terms of the use rate measures of Table 1, this would give rates upwards of 900%. Jank (1987) has found that the capacity of a waste treatment plant can be effectively doubled through the use of computerized controls of plant processes. The energy savings possible through the use of water efficient fixtures has already been mentioned. Research at Environment Canada has shown that petroleum-like material can be recovered from waste treatment plant sludge. Changing industrial systems with water handling as a design criterion is effective in both saving water and lowering costs (Ayers and Kneese, 1968). These are but a few of many examples of technological change possible in the water industry.

4. THE ROOT OF THE CONUNDRUM: WATER VALUATION

It was suggested earlier that economic forces have not been at work in the water resources field. This almost complete failure to use market forces in helping to allocate water resources lies at the root of the retardation of technological in the water industry. This section presents two examples which illustrate this lack of attention to economic factors.

(Before going any further, one point is important in qualifying the argument presented here. The operation of an unfettered market is not always superior, and, in the environmental case, some mix of regulation and incentive is probably the best approach. However, the power of market forces offers great advantages, which have to be recognized by the water management profession.)

Environment Canada has conducted a number of surveys of retail prices to the users of municipal water services across Canada. These surveys were undertaken to establish some baseline information on the conditions faced by water consumers. In other words, what are the "signals" being received by consumers about the value of water services?² The results of these surveys have interesting economic implications for the problem posed in this paper.

The surveys show that about one-third of the price structures in use by Canadian municipalities comprise what are commonly referred to as flat rates. The cost of an extra, or marginal, unit of water under this type of structure is zero. In other water becomes a free good, and used accordingly in a wasteful manner, regardless of the need to conserve.

Most of the other structures in use are termed declining block rates, under which the price of water declines progressively with increasing use. The rationale for this type of structure, clearly stated by the A.W.W.A. (1983), has been discredited in much of the professional literature (Hirschleiffer et al., 1960; McNeill, 1987). The remaining structures are constant unit charges (i.e. a constant price per unit of use, regardless of quantities used), increasing block rates or some other more complex types of arrangements

Thus, a first major observation is that price structures actually encourage overuse of public water supplies. This has been witnessed by the elevated costs of supplying water and waste treatment services, and the consequent overbuilding of water facilities. The

²Note that these surveys made no attempt to link consumer prices to the costs of providing the service. Thus, definitive judgements about whether water prices are effective in terms of cost recovery cannot be made from the data collected.

current financial problems in the municipal water industry (FCM, 1985) are hardly surprising under these conditions. Worse still is the almost complete absence of incentives for technological change in the industry today.

This situation is compounded when the unit prices for water (where these are relevant) and total retail prices are examined (Table 2). Three observations are relevant here. First, unit, average and total prices are very low in comparison with the prices of other goods and services. For example, the cost of a cubic meter of soft drink, the next cheapest common liquid in use is about \$500.00. Second, the price of water includes delivery to the home and waste removal. Third, prices have increased over the three-year period covered by the table, but are still relatively insignificant in relation to the costs of other services, such as electricity. The "signal" being passed to consumers, accordingly, is that the service is cheap to produce, and that waste is an insignificant problem.

The second example is drawn from the 1981 and 1986 industrial water use surveys, conducted nationally, covering about 7,000 industrial establishments (Tate and Scharf, 1985, 1989). Water costs to industry totalled \$421 million in 1981 and \$585 million in 1986 (current dollar terms). In both cases, these amounts were under 1% of total production costs. In irrigated agriculture, water costs are subsidized 85%-90% by public agencies, which construct the infrastructure, charging irrigators low flat charges per hectare for the actual commodity. In these cases, again, water prices are insufficiently low to provide incentives for rational water use and for technological change.

5. INTERPRETATION AND CONCLUDING REMARKS

The data provided in this paper show that Canadian water prices are very low. The implication for water use in a static situation is one of overuse, both in a quantitative sense, and in the sense of cheap or free use of water courses for waste removal. Dynamically, low prices mean that little or no account is taken of economic factors in forecasting water demands, resulting in forecasts which are biased upward and resultant overbuilding of systems.

Low prices also mean that cost recovery is not achieved. One implication here is that capital shortages frequently occur and that other public infrastructure often take precedence over water infrastructure. The municipal infrastructure financing problem identified by FCM (1985) is therefore not surprising.

Of most relevance for this paper is that current economic practices provide no incentive for capital-driven technological change. For instance, the industry is unable to attract the voluntary research funds, which are critical for technological change. The industry

is critically in need of technological upgrading, similar to that which has occurred in connection with the energy industry, an equally important infrastructural element. However, in contrast to that industry, there are few economic incentives in water. We can confidently predict that few of the needed changes will occur until economic practices are radically reformed.

Table 2 Selected municipal water price indicators, Canada, 1986 and 1989

Indicator	1986		1989	
	Canada	Ontario	Canada	Ontario
a. Unit prices (cents/m ³)				
1. CUC	38	40	52	65
2. BR-first	48	43	62	57
3. BR-last	29	24	39	41
b. Retail prices (\$/month)				
1. 10 m ³ /month	10.90	11.49	14.40	15.96
2. 25 m ³ /month	14.77	15.10	18.15	21.00
3. 35 m ³ /month	16.08	17.39	20.88	24.57
c. Average prices (cents/m ³)				
1. 10 m ³ /month	109	115	144	160
2. 25 m ³ /month	59	60	73	84
3. 35 m ³ /month	46	50	60	70

Notes: CUC = constant unit charge.
 BR-first = price per m³ in the first block.
 BR-last = price per m³ in the last block.

NOTE: All prices include the relevant sewer surcharges.

Sources: Tate (1989); Tate and Lacelle (1990)

REFERENCES CITED

- American Water Works Association (1983). Manual of water supply practices: water rates. Denver, AWWA M1.
- Ayers, R and A.V. Kneese (1966). The Economics of Water Utilization in the Beet Sugar Industry. Baltimore: Johns Hopkins Press
- FCM (Federation of Canadian Municipalities) (1985). Municipal infrastructure in Canada: physical condition and funding adequacy. Ottawa-Hull.
- Hirschleifer, J., J.C. de Haven and J.W. Milliman (1960) Water supply: economics, technology and policy. Chicago: University of Chicago Press.
- Jank, B., (1987). Personal communication
- Kollar, K.L. and Macauley, P. (1980). "Water Requirements For Industrial Development". Journal, A.W.W.A., 72, #1, pp. 2-9
- McNeill, R. (1989). The Economic Theory of Water Pricing. Vancouver: Environment Canada, Inland Waters Directorate, Pacific and Yukon Region.
- Patry, G. and I. Takacs (1990). "Assessing the Effects of Hydraulic Load Reductions on Wastewater Treatment Plant Performance". Hamilton: McMaster University, unpublished study completed under contract for Environment Canada.
- Pearse, P.H. and D.M. Tate (1990). "Economic Instruments for Sustainable Development of Water Resources". Victoria, B.C.: Westwater Research Centre (a paper prepared as a chapter of a book on sustainable development in the Fraser River basin), publication pending.
- Postel, S. (1985). "Conserving Water: The Untapped Alternative", Worldwatch Paper 67, September 1985.
- Schmookler, J. (1966). Invention and Economic Growth. Cambridge, Mass.: Harvard University Press.
- Solow, R. (1957). "Technical Change and the Aggregate Production Function". Review of Economics and Statistics, 39, 312-320.
- Tate, D.M. (1984). "Canadian Water Management: A One-Armed Giant". Canadian Water Resources Journal, 9, #3, pp. 1-7.
- Tate, D.M. (1988). "Municipal Water Rates in Canada: Current Practices and Prices". Ottawa-Hull: Environment Canada, Inland Waters Directorate, Social Science Series 21.

Tate, D.M. and D.N.Scharf, (1985). "Water Use in Canadian Industry: 1981. by Ottawa-Hull: Department of the Environment, Inland Waters Directorate. Social Science Series, 19.

Tate, D.M. and D.M. Lacelle (1990) "Municipal Water Rates in Canada: Current Practices and Prices, 1989". Ottawa-Hull: Environment Canada, Inland Waters Directorate, Social Science Series, publication pending

Tate, D.M. and D.N.Scharf, (1990). "Water Use in Canadian Industry: 1986. Ottawa-Hull: Department of the Environment, Inland Waters Directorate. Social Science Series, publication pending.

MODELLING MUNICIPAL WATER SYSTEMS FOR DEMAND MANAGEMENT

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INTRODUCTION

Water demand management is something not extensively practised by Ontario municipalities (Kreutzweiser & Feagan, 1988), therefore it is best placed in the context of the prevailing water management philosophy. Traditionally most demands for water have been viewed as legitimate so that municipalities generally feel that they must provide water for all users and for all purposes. This is the philosophy of supply management and it is reinforced by the perception that this province has an abundance of water. Although this may appear true, the annual runoff into the Great Lakes is only 1% of their volume; also, local population densities and degradation of water quality can and do lead to short and/or long term shortages of water. In addition, it is usually assumed that water provision is relatively inexpensive. Even if this were the case, the implied costs of providing wastewater treatment are rarely considered in a decision to expand water supply, yet few would consider those costs unimportant. Supply management practised alone can lead to overinvestment in structural solutions (pipelines, sewage treatment plants, etc.) to water problems. Demand management seeks to modify the amount of water demanded rather than the amount of water supplied. It is becoming increasingly attractive for economic and availability reasons and also because the issue of water resource allocation is involved. Water not used by municipalities is water available for other uses, particularly in-stream or in-situ uses, e.g. for maintaining aquifer levels for the benefit of the agricultural community.

The Regional Municipality of Waterloo is currently facing short term water shortages in the Tri-City area (Kitchener, Waterloo and Cambridge) due to growth of population and industry. The supply augmentation project under construction will provide water at many times the cost of water from current sources. Also, part of the water supply of Kitchener-Waterloo currently comes from aquifers situated in the surrounding rural municipalities, who are concerned that water withdrawals by the cities are lowering water table, to the detriment of the farming community. Also, the contamination of the Elmira water supply by DMNA is putting further stress on the Tri-City area water supply, since a pipeline is being built from Waterloo to Elmira for the purpose of supplying Elmira's needs.

This study is developing a model of the water system which can be used by a municipality to examine the potential for and the cost effectiveness of demand management. Such a model should integrate the supply and distribution of water, usage of water and the collection and treatment of wastewater (Robinson & alia, 1984).

GENERAL SYSTEMS MODELLING SOFTWARE: STELLA

Modelling was done with STELLA (Richmond & alia, 1987), a general systems modelling application for MacIntosh microcomputers. MacIntoshes computers can now read and write to IBM formatted diskettes, so that input from and output to the IBM environment is now practical. In STELLA, model variables are represented by graphical elements. These elements are laid out on the computer screen as in a

computer drawing application. An example of a simple model is shown in Figure 1. In this example, the variable "served_population" is derived from integrating "population_growth" over time, and is therefore represented by a rectangular element, called a stock. The circular elements, representing constants, algebraic formulas or graphical functions, are called converters.

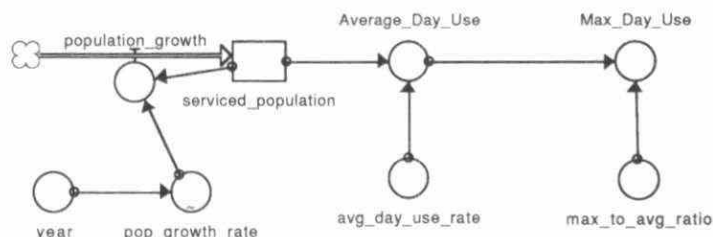


Figure 1. A simple model for forecasting water demand.

In STELLA, all inputs from one element to another, whether of quantities being modelled or of information, are indicated graphically. For example, average day use is a function of serviced population and average day use per capita. Arrows are therefore placed to indicate this. After the arrows are placed, the nature of the dependence is qualified either by an algebraic expression, or by a graphical function. "Pop_growth_rate" in this example is a graphical function of "year". STELLA then generates an equation file automatically from the diagram. Table 1 gives the equation file for this example.

Output from a STELLA model can be obtained in tabular or graphical form of both. Using STELLA models, revised input data can be used to quickly generate revised forecasts. The numerical integration capability of STELLA makes it particularly useful for forecast modelling.

• EXAMPLE 1: REGIONAL MUNICIPALITY OF WATERLOO: WATER SUPPLY

In the Tri-City area of the Regional Municipality of Waterloo, water is currently supplied from wells. Due to growth in population and industry, the current supplies will soon become inadequate. In fact, lawn watering bans have imposed frequently in recent years in order to reduced maximum day demand. A Master Water Supply Study was completed for the Region by M.M. Dillon, an engineering consultant, in 1987. The Master Water Supply Study considered various options for future sources of water supply, and recommended an aquifer recharge scheme, which involves abstracting water from the Grand River and using it to recharge the aquifer at Mannheim. The implementation of this scheme will involve several phases. As each phase is initiated, the available water supply will increase in stepwise fashion. Construction is well under way on the first phase.

Data from the Master Water Supply Study was used in a model of water use and supply for the Tri-City area. Such a model is ideal for the determination of when new

Table 1. Equation file from the model of Figure 1.

```

serviced_population = serviced_population + dt *(population_growth)
INIT(serviced_population) = 200.000
{Units: thousands of people}
Average_Day_Use = avg_day_use_rate*serviced_population/1000
{Units: millions of gallons per day}
avg_day_use_rate = 100
{Units: gallons per person per day}
Max_Day_Use = max_to_avg_ratio*Average_Day_Use
{Units: millions of gallons per day}
max_to_avg_ratio = 1.5
{ratio of maximum day use to average day use}
population_growth = (pop_growth_rate/100)*serviced_population
year = TIME
pop_growth_rate = graph(year)
(1986.000,3.390),(1991.000,2.025),(1996.000,2.250),(2001.000,2.575),(20
06.000,1.600),(2011.000,1.800),(2016.000,1.930),(2021.000,1.630),(2026.0
00,1.400),(2031.000,2.750),(2036.000,1.100)

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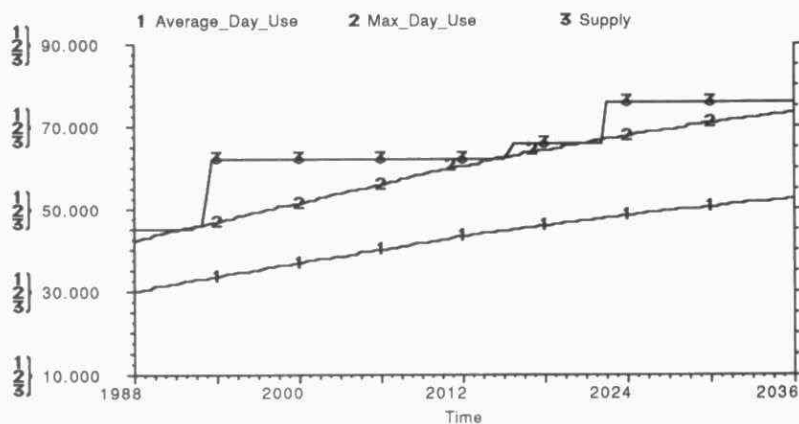


Figure 2. Water supply forecast for the Tri-City area of Waterloo Region illustrating the steps in water supply growth as controlled by maximum day use.

water supplies will be required. The word "required" used in this sense is a relative term which is dependent on the assumptions of the model with regard to water conservation options. Typical output of this STELLA model, in graphical form, is shown in Figure 2.

• EXAMPLE 2: EFFECT OF PRICE ON WATER DEMAND

The Master Water Supply Study contained recommendations for capital expenditure on water supply development which will result in increases of the real cost of water by a more than factor of three in less than a decade. The study presumed that no changes in overall water use or in the pattern of water use would result from price increases. A model was constructed to be able to evaluate the effect of price on water demand, and thus on the need to develop additional supplies. It was assumed that prices are set to cover expenses, at least in the long run. Thus demand is a function of price, but also price is a function of demand. The STELLA modelling application is particularly well suited to handling this type of mutual dependence.

Typical output of this model is shown in Figure 3. The presentation in Figure 3 is for illustration purposes only, since data on the price elasticity of water demand in Waterloo Region is not available and because in this particular model price increases occur only after capital expenditures. In practice, Waterloo Region smooths out such price increases by raising rates in anticipation of expenditures. Figure 3 shows that price increases can be expected to depress water use and delay capital expansion (compare Figure 2).

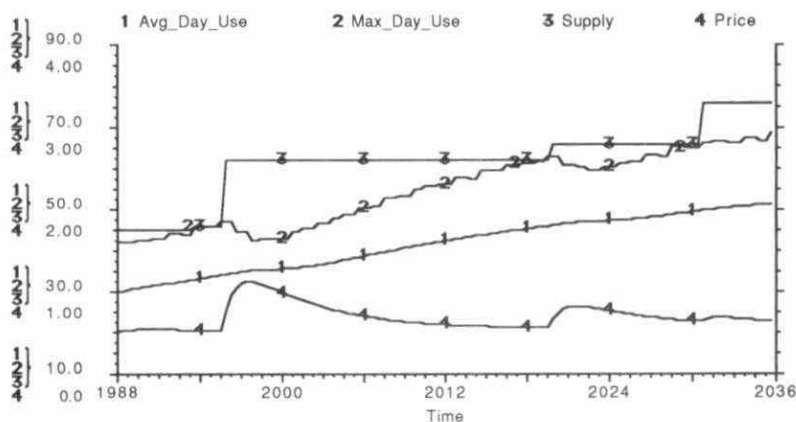


Figure 3. Water supply forecast illustrating the interrelated effects of price and water use.

• EXAMPLE 3: INTEGRATION OF WATER SUPPLY AND WASTE-WATER TREATMENT

Full implementation of the Master Water Supply Study will require abstractions of Grand River water at a rate possible only if substantial changes are made in wastewater treatment facilities. The study did not, however, consider the effects of the implied facility expansions, some of which might not be required, or might be delayed, if greater efforts at managing water demand were instituted.

In order to consider such effects, an integrated model of all water supply systems and waste water treatment systems in the Regional Municipality of Waterloo was constructed. This is the largest model to date, consisting of about 175 model elements. Because of its complexity, a custom-made user interface was designed¹. The output of this model therefore looks different from that of previous models. A sample of its output is shown in Figure 4, which illustrates waste-water treatment of the City of Waterloo and allows comparison with water use. The excess waste-water treated at the Waterloo sewage treatment plant comes from inflow and infiltration into the sanitary sewer system. Note that the plant expansion of 1989 would not have been necessary if inflow and infiltration were reduced.

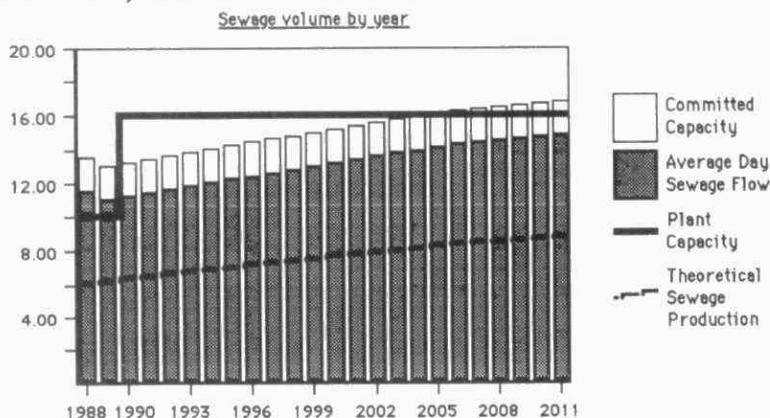


Figure 4. Wastewater treatment forecast for the City of Waterloo. All units Committed capacity refers the required treatment capacity if all approved housing units were to be built. Theoretical sewage production was set at 85% of average day water sales in the service area.

DISCUSSION

The goal of this study is to produce a model that integrates water supply with wastewater treatment in a way that promotes the use of demand management. The model is being developed to have immediate applicability in the Regional Municipality of

¹The interface was designed in HyperCard using STELLAStack from High Performance Systems.

Waterloo, where it would be useful for evaluating the cost effectiveness of water demand management practices and policies, as well as predicting timing of expansion of water supply and waste water treatment systems. With further development, the model could have more general applicability to municipalities across the province.

The model should be very useful both to consulting firms and to municipalities. While many people are aware of the concept of demand management, the application to water supply and wastewater treatment planning is not well understood at present. In addition, a further study to determine the effect of climate change on water demand and supply is planned.

REFERENCES

Kreutzwiser, R.D. & R.B. Feagan. 1988. Municipal Utilization of Water Demand Management Strategies in Ontario Municipalities. *Proceedings of Technology Transfer Conference 1988*. Environment Ontario.

Richmond, B., Peterson, S. & Vescuso, P. 1987. *An Academic User's Guide to STELLA™*. High Performance Systems, Hanover, New Hampshire.

Robinson, J.E., J.E. Fitzgibbon & B.A. Benninger. 1984. Integrating Demand Management of Water/Wastewater Systems: Where Do We Go From Here? *Canadian Water Resources Journal* 9(4).

**ECONOMIC ANALYSES OF ONTARIO'S WATER POLLUTION CONTROL
INITIATIVE FOR DIRECT INDUSTRIAL DISCHARGERS**

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ABSTRACT

Economic analyses have played, and will continue to play, an important role in assessing the potential incremental financial and economic consequences of monitoring and abatement requirements. The purpose of the present paper is to present the results of the economic and financial analyses of the various MISA regulations that have been developed or promulgated for direct industrial dischargers, and to identify major economic issues associated with the MISA program and describe how they have been resolved or addressed with respect to industrial direct dischargers.

OVERVIEW OF THE MISA PROGRAM

The Municipal-Industrial Strategy for Abatement (MISA) program was announced by the Government of Ontario in June 1986 (MOE, June 1986), and is intended to achieve the "virtual elimination of toxic contaminants in municipal and industrial discharges into (provincial) waterways" (MOE, June 1986, p.7). To this end, regulations are being developed which require industrial plants that discharge wastewaters directly into provincial waterways to monitor their effluents intensively and, ultimately, reduce the loadings and/or concentrations of certain contaminants to specified limits. These limits are to be determined according to the "Best Available Technology, Economically Achievable" (BATEA) that is specific to each particular industrial sector.

The MISA program encompasses over 300 mines and industrial establishments in Ontario which discharge their wastewaters directly into provincial waterways. These direct dischargers are disaggregated into nine industrial sectors for which monitoring and effluent Limits will be developed:

- | | |
|----------------------|-----------------------|
| - petroleum refining | - industrial minerals |
| - organic chemical | and manufacturing |
| manufacturing | - electric power |
| - pulp and paper | generation |
| - iron and steel | - inorganic chemicals |
| - metal mining and | - metal castings |
| refining | |

¹Municipal sewage treatment plants and the industrial plants that discharge wastewaters to them will be incorporated into the program by means of several regulatory activities.

Joint Technical Committees (JTCs) have been established for each MISA industrial sector (and for municipal sewage treatment plants). These Committees are comprised of provincial, federal and industry representatives who agree upon the actual regulations. The draft regulations and other components of the MISA program are also reviewed by the MISA Advisory Committee.

A program² of economic investigations has been carried out in support of the MISA program and to fulfil Ontario Government requirements to evaluate the socio-economic implications of major regulatory initiatives and to provide such information to responsible Government authorities.

MISA ECONOMIC PROGRAM

A program of economic studies has been initiated to generate the required information and to complement technical assessments and regulation development efforts. The objectives of the economic program (MOE, June 1987) are:

- a) to develop an economic database for those industrial sectors which will be subject to MISA monitoring and effluent limits regulations;
- b) to develop estimates of the costs of proposed monitoring and effluent limits regulations for each industrial sector and for municipalities;
- c) to determine the economic effects and consequences of these costs;
- d) to develop criteria with which to define BATEA;
- e) to design implementation programs that will achieve the MISA goals and objectives at least cost;
- f) to contribute to the design of more effective policies and programs to control sewer uses by industrial dischargers; and
- g) to provide information about the beneficial consequences of the various monitoring and abatement requirements including changes in the risk of certain health effects.

The economic program began with the preparation of industrial economic profiles for each sector. These profiles

²This program is described in MOE (1987), and Salamon and Donnan (1988).

include physical and economic data, financial performance ratios, current trends, and forecasts of future market production and consumption trends. Following the production of these economic profiles, studies were carried out to estimate the costs of the proposed monitoring requirements for each sector and on individual firms and their plants, and to assess the economic and financial implications of these costs. These evaluations have aided Ministry personnel and the JTC in determining the most cost-effective methods of monitoring for selected contaminants. The cost of monitoring studies also identified those firms or plants which might be unduly affected by the regulatory requirements.

After each 12-month monitoring period, effluent limits regulations for each direct discharge sector will be developed. Abatement technologies to achieve MISA objectives will be identified and related costs estimated for each industrial sector. A key objective will be to find combinations of technologies that will achieve the MISA objectives at least-cost and to define criteria to help judge what is "economically achievable".

EFFORTS TO DEFINE "ECONOMIC ACHIEVABILITY"

UNITED STATES EXPERIENCE³

In the United States, the authority to consider the economic consequences of regulatory requirements is found in statutes and executive orders, many of which apply to the U.S. Environmental Protection Agency (USEPA). Under the U.S. Clean Water Act, the USEPA rule-making activity is to establish effluent limitation guidelines for industrial and municipal wastewater treatment facilities. The Clean Water Act states that such effluent limitations will require "application of the best available technology economically achievable ...", but does not define the term. In fact, the concept of BATEA appears only once in U.S. statute, and that is in the Clean Water Act. Other environmental statutes make broad reference to economic considerations, but do not specify how they are to be measured.

While there is no explicit definition of 'economic achievability', the USEPA, based on the U.S. Congressional record and the language of the U.S. Clean Water Act, has interpreted salient Acts to mean that the primary measures of "economic achievability" for private sector regulated parties are plant closures and job loss. In practice, the USEPA has used a variety of financial measures as predictors of plant closures and job losses. Such measures differ for the private and public sectors.

³This section is based on the results of a study by Peat Marwick (1990).

Economic impact studies of proposed regulations on private industrial sectors included calculation of the effect of incremental compliance costs on the financial statements of affected firms and, where data were available, on the cost structures of individual plants. The potential number of plant closures were inferred from these calculations.

Assessments in the United States are often tailored to focus on small business. The analytical framework is not changed, but impacts on small business are identified and the implications of less stringent control requirements for small firms are discussed.

USEPA economic studies employ a number financial ratios and cash flow analyses to estimate economic impacts. In earlier studies, the USEPA found that financial ratios can be grouped into four basic categories:

- profitability
- liquidity
- solvency
- efficiency

In its analysis, the USEPA sought to ensure that a suitable test for assessing economic impacts should possess strong empirical justification, have sufficient historical data, and can be simple and consistent to apply to available data. However, a review of sectoral economic impact studies shows that there was no consistent, rationale application of the concept of "economic achievability". For example, in the U.S. Foundry sector, firm-level financial ratios were used to predict plant closure because of the large number of plants and the resulting difficulty in gathering industry-wide plant-specific data. The three financial ratios used, which satisfied requisite criteria were: return on assets, total debt to total assets, and cash flow to total debt. Conversely in the Organic Chemicals and Non-Ferrous Metals Manufacturing sector studies, the USEPA utilized a discounted cash flow analysis.

In summary, there is no single definition or consistent application of the concept of "economic achievability" from the United States. This meant that the Ministry of the Environment must develop requisite principles, procedures and criteria to use as a framework for carrying out assessments of economic achievability for entities subject to MISA.

ONTARIO ECONOMIC ACHIEVABILITY ASSESSMENT⁴

Economic and financial assessments in support of MISA Limits Regulation development for each industrial sector will consist of four primary areas of focus. These principles and procedures are based on accepted economic theories which provide a framework for the analyses and comparisons of alternative BAT options.

Cost-Effectiveness Analyses

Cost-effectiveness analyses compare costs of different BAT (best available technology) Options with loadings of relevant pollutants to determine least-cost and cost-effectiveness of each BAT Option. Such analyses will show the distribution of costs among plants.

To the extent possible, abatement costs for relevant BAT (best available technology) options are to be estimated for individual plants subject to the MISA regulations. Types of cost information that are expected to be assembled for each sector in order to develop such BAT cost estimates include:

- (a) pollutant removal efficiencies, variables that may affect the efficiencies, and operational reliability;
- (b) capital costs relevant to the type and scale of each abatement technology at the plant capacity;
- (c) operating and maintenance costs;
- (d) operating life of abatement technologies; and
- (e) private benefits of each BAT option, including reduced energy or materials inputs, saleable by-products, reduced labour requirements, and enhanced production efficiencies.

In order to compare or to sum net costs among plants, cost estimates will be converted to either annualized costs or to discounted present values. Such conversions permit one-time capital expenditures for equipment that lasts for a number of years to be considered simultaneously with annual operating and maintenance expenses.

⁴As a prelude to the development of Limits Regulations, the Ministry identified 18 "issues of concern" and established committees comprising Ministry staff, stakeholder agencies, industry, municipalities and the MISA Advisory Committee to address these issues. The results have been published and circulated for public input. The issue of "economic achievability" is discussed on pp.97-148 (MOE, June 1990).

These cost estimates will be displayed as abatement cost functions, which are relationships between different levels of contaminant removal at a pollution source and the minimum cost of achieving them. Abatement cost functions generally display only the least-cost combinations of technologies to achieve specific degrees of removal or final loadings. The least-cost combination of compatible abatement technologies to achieve a given degree of pollutant removal is a "cost-effective BAT option". The development of up to four BAT options (i.e. four levels of water pollution abatement) will provide a clear range of cost-effective BAT options for economic achievability assessments.

Ability of Firms and Sector to Pass On Incremental Abatement Costs

Cost increases can be more easily passed along to consumers to the extent that a firm has a greater degree of monopoly power in its product market. Likewise, cost increases can be more easily passed back to suppliers to the extent that a firm has a greater degree of 'monopsony' power (i.e. when a buyer faces limited competition from other purchasers). In a competitive market, cost increases could be passed on to consumers in higher prices as more firms in the industry are subject to higher costs. However, if only a few firms in a market incur higher costs, owners of these firms are more likely to experience reduced profits.

Financial Impact Analyses of Incremental BAT Option Costs on Firms (and Plants) and Sector if Prices Cannot be Raised

Estimated incremental costs of monitoring were evaluated in relation to three financial indicators of subject firms:

- a) return on investment or capital employed;
- b) ratio of operating cost to after-tax profits; and
- c) proportion of incremental capital cost to firm's historical capital expenditures.

Building on these analyses and the experience from the United States, it is proposed that financial indicators and tests applied to proposed MISA Limits requirements should be directed at assessing the consequences for plants (if data are available), individual firms, industrial sectors, and the provincial economy as a whole. Assessments should also be implemented to determine if there are disparities of effects between large and small businesses and between regions within the province. It must be noted that there are no widely agreed upon threshold ranges for any of the potential performance indicators.

Financial indicators of a firm (or plant) will be affected if the costs of abatement, in part or in entirety, cannot be

passed on in some form. To the extent possible, analyses will explicitly show distribution of effects on firms (owners, employees), industrial sectors, and the provincial economy (consumers, sub-provincial regions, and small business).

Competitive Analyses on Firms (and Plants) and Sector if Prices Cannot be Raised

Competitive analyses involve an assessment of the operating costs of abatement relative to the position of the firm (or plant if data are available) and Sector in relation to domestic and international competitors.

COSTS AND IMPLICATIONS OF MONITORING REGULATIONS

ESTIMATED COSTS OF MONITORING

Estimates of the potential incremental costs to each plant subject to MISA monitoring requirements were calculated and published for each industrial sector. The reports also presented estimates of the economic and financial effects of the monitoring costs on each sector, subsector(s), and where possible, on individual firms. Publicly available information were used for these assessments. Ministry staff wrote to affected plants requesting the provision of plant-specific data with to conduct more salient economic analyses. However, the majority of plants felt that such information was proprietary in nature.

Incremental costs of monitoring consist of recurring operating and maintenance costs and one time capital and installation costs. In many instances, capital cost estimates were calculated by individual plants and supplied to the Ministry for incorporation into the economic assessments. The sectoral Regulations specified requirements for each of the monitoring activities for each plant. Cost-effectiveness of the monitoring requirements were examined by comparing the costs associated with the proposed monitoring requirements to the potential costs that would be incurred under alternative requirements. It was found that the incremental costs of monitoring would be much higher under the alternative scenarios.

Table 1 illustrates the capital, operating and total estimated incremental costs for each of the industrial sectors. The MISA monitoring requirements were estimated to cost \$73.7 million in total, or an average of \$307 thousand per plant. Draft versions of the cost of monitoring reports were issued for public and industry review and comment along with the Draft Monitoring Regulations. Subsequent comments were incorporated into the final versions of each report.

ACTUAL COSTS OF MONITORING

As a follow up exercise, the Ministry has developed a questionnaire, with assistance from 27 industrial representatives, in order to compile information on the actual costs and potential benefits of monitoring incurred by plants subject to the MISA monitoring requirements.

TABLE 1
.....
TOTAL ESTIMATED INCREMENTAL COSTS OF
MISA MONITORING REQUIREMENTS

SECTOR	# OF PLANTS*	(S THOUSANDS)		AVERAGE COST	
		CAPITAL	OPERATING	TOTAL	PER PLANT
PETROLEUM REFINING	7	\$1,575.0	\$2,081.0	\$3,656.0	\$522.3
ORGANIC CHEMICAL	19	\$2,812.0	\$8,046.5	\$10,858.5	\$571.5
IRON & STEEL	7	\$5,120.9	\$3,250.2	\$8,371.1	\$1,195.9
INORGANIC CHEMICAL	22	\$1,485.7	\$4,106.1	\$5,591.8	\$254.2
METAL MINING	67	\$3,938.0	\$14,067.0	\$18,005.0	\$268.7
PULP & PAPER	27	\$3,697.2	\$5,545.0	\$9,242.2	\$342.3
METAL CASTING	13	\$535.0	\$804.0	\$1,419.0	\$109.2
ELECTRIC POWER	27	\$6,095.1	\$8,515.1	\$14,610.2	\$541.1
INDUSTRIAL MINERALS **	51	\$316.5	\$1,666.6	\$1,983.1	\$38.9
TOTAL:	240	\$25,575.4	\$48,161.5	\$73,736.9	\$307.2

* Number at time of Monitoring Regulation promulgation.

** Sector contains about 130 plants. However, of the about 100 quarries, only 20 are being monitored as representative of the quarry subsector. All 100 quarries are sharing the costs of monitoring.

Source: MOE, Policy and Planning Branch

The questionnaire was distributed in June 1990 to over 300 plants subject to the MISA monitoring regulations. Participation in this exercise is entirely voluntary. Information will be received over the next year as each sector completes its monitoring requirements. To date, information has been received from all 7 plants within the Petroleum Sector.

The information collected will be used to document the actual cost and beneficial consequences of monitoring and to improve future planning and cost estimation activities. Information contained in the questionnaire will be compared with the estimated costs of monitoring in order to:

- estimate the margin of error for both capital and operating cost estimates;
- analyze reasons for discrepancies in estimates; and
- analyze the accuracy of assumptions used in the estimation of incremental monitoring costs.

Information on details such as equipment costs as a percentage of total costs, labour costs as a percentage of total costs, and an understanding of any interrelationship between costs and physical attributes (such as flow and capacity) will improve the Ministry's ability to estimate costs of concurrent and future environmental initiatives, as well as to critically review industry cost estimates. Finally, such information will provide additional background information about each plant's operation, such as the appropriate contact person, current employment levels, major products, plant capacity, and plant location.

Table 2 presents preliminary results of the estimated and actual capital and operating costs by monitoring activity for the Petroleum Sector. As indicated in Table 2, the total actual costs of all monitoring activities were 151% higher than the estimated costs. It is interesting to note that it is the reporting activity where the largest variance occurred, with the actual total costs being almost four times greater than the estimated costs.

Actual capital costs were 50% higher than the estimated capital costs, while actual operating costs were just over 40% greater than the estimated costs. These preliminary results suggest that the variance for both operating and capital costs is in large part due to the divergence of the actual and estimated costs for the reporting activity.

TABLE 2
TOTAL ACTUAL INCREMENTAL CAPITAL AND OPERATING COSTS OF MISA MONITORING
AS REPORTED BY THE
PETROLEUM REFINING SECTOR
(\$ Thousands)

Monitoring Activity	Capital Costs		Operating Costs		Total Costs		Percent Difference Actual/Estimate
	Estimate*	Actual	Estimate	Actual	Estimate	Actual	
Sampling	486.0	999.5	285.3	367.9	771.3	1,367.4	77%
Flow Measurement	712.0	994.2	58.0	18.2	770.0	1,012.4	31%
Analytical Testing	315.0	339.9	1,066.6	605.3	1,381.6	945.2	(32%)
Reporting	42.0	102.2	120.0	544.4	162.0	646.6	299%
Consultant Contracts	0.0	0.0	0.0	676.7	0.0	676.7	-
TOTAL	<u>1,555.0</u>	<u>2,435.8</u>	<u>1,529.9</u>	<u>2,212.5</u>	<u>3,084.9</u>	<u>4,648.3</u>	<u>51%</u>

* SOURCE: MDE, July 1988

Information from the questionnaire also revealed that each plant engaged at least two separate consultant contracts to perform monitoring activities for a total of 23 separate contracts for the sector. Although some consultants were hired for more than one monitoring activity, over 50% of the costs for consultant contracts were for analytical testing. The questionnaire results also indicate that only a small amount of additional employment was generated by the monitoring requirements. Just 3.5 permanent full time employees and 3 temporary employees were hired in the entire Petroleum Sector to aid in fulfilling monitoring requirements.

The only beneficial effects noted was that computer equipment purchased for monitoring could be used for other activities.

COST ANALYSES OF BAT OPTIONS FOR THE ONTARIO PETROLEUM REFINERY SECTOR

Preliminary capital and operating cost estimates and pollutant removal efficiencies of specific pollution control technologies⁶ for each plant in the Petroleum Sector have been prepared. The cost estimates were adjusted to each refinery on the basis of the average recorded flow rate recorded during the monitoring period. These cost and pollutant removal estimates are illustrative and do not necessarily represent the technologies that will ultimately determined to be BAT.

The application of two sets of BAT Options to each refinery show that the potential capital costs of applying the two available BAT Options range from \$0.6 million to \$42 million per plant while incremental O&M costs could range from \$0.3 million to \$3.5 million per year. Total capital costs for the Sector range from \$125.5 million to \$130 million. Total annualized costs, over 10 years, could range from \$25.2 million to \$27.2 million. These wide ranges in potential costs among each refinery are the result of the wide range of flows and contaminant levels found in effluents in each refinery.

⁵This section relates to preliminary analyses contained in VHB (forthcoming). Cost estimates will be refined pending subsequent studies.

⁶These estimates are based on 3 potential Petroleum Sector-specific BAT Options (end of pipe filtration technologies): GMF (granular media filtration), GAC (granular carbon adsorption), and PAC (powdered activated carbon) filters. (VHB 1990) notes that these technologies will remove only 8 parameters: oil and grease, total organic compounds (TOC), total suspended solids (TSS), zinc, chromium, benzene, phenols and toluene.

The analyses indicate, taking into account some uncertainty regarding technical removal efficiencies, that the GAC-GMF BAT Option is more cost-effective in that it potentially removes more kilograms per year of all pollutants from the refineries than the PAC-GMF BAT Option.

The analyses is complicated by the fact that each BAT Option removes different pollutants at different levels of abatement. This makes defining and setting Limits difficult. One approach would be to define the best potential loading reduction achieved by each BAT Option in each refinery as the Limit. This means that each refinery would be in compliance as long as it achieves the best reductions permitted by the BAT Options for each contaminant that is possible at the particular refinery. Another approach would be to set the individual contaminant loading Limits and the lowest achieved by an Ontario refinery. This, however, may not be achievable for each contaminant of concern.

A third option is to define the Limit in terms of loadings per unit of production. A Petroleum Sector Limit would be defined as a maximum loading of a contaminant (in kilograms or tonnes per unit time) per cubic metre of crude oil processed. This definition would allow for the large differences in crude processing capacities of Ontario refineries.

As noted, these analyses are illustrative and indicate the types of analyses that will be carried out during the development of the MISA Limits Regulations. It should be emphasized as well that other important factors will also be considered in the final determination of Limits and other regulatory requirements.

CONCLUSIONS

Economic assessments will continue to be an integral part of the MISA and other Ministry environmental policy initiatives. Financial and economic analyses to-date indicate that these costs will not likely compromise the economic or financial viabilities of the sectors or the individual firms for which financial data were available. Concurrent studies (Hickling 1990, Ernst & Young 1990) have further indicated that Ontario's environmental agenda poses no major competitive disadvantage vis a vis other jurisdictions.

REFERENCES

- Donnan, J. et al, "Abatement Cost Functions - the Workhorse of Environmental Management", in Proceedings of 1986 Technology Transfer Conference, MOE 1986
- Ernst & Young Management Consultants, Implications of Business Combinations for Environmental Protection, Prepared for MOE, Policy and Planning Branch, May 1990
- James F. Hickling Management Consultants, The Regulation of Industrial Toxic and Hazardous Emissions in Ontario as Compared With Selected Jurisdictions, Prepared for MOE, Policy and Planning Branch, January 1990
- Ontario Ministry of the Environment, "Cost Estimates and Implications of the 'Effluent Monitoring - General' and 'Effluent Monitoring - Petroleum Refining Sector' Regulations for Ontario's Petroleum Refineries", Policy and Planning Branch, July 1988
- Ontario Ministry of the Environment, "Economic Information Needs and Assessments for Developing MISA Monitoring and Abatement Requirements", Policy and Planning Branch, March 1987
- Ontario Ministry of the Environment, "Effluent Monitoring Regulations for the Petroleum Refining Sector", July 1988
- Ontario Ministry of the Environment, "MISA Issues Resolution Process - Issue Resolution Committee Reports", June 1990
- Ontario Ministry of the Environment, "A Policy and Program Statement of the Government of Ontario on Controlling Municipal and Industrial Discharges into Surface Waters" (MISA "White Paper"), June 1986
- Peat Marwick Management Consultants, Review and Analysis of Economic Achievability Assessments of Environmental Protection Expenditures, Prepared for MOE, Policy and Planning Branch, 1990
- Salamon, Orna E. and Donnan, Jack A., "Economic Assessments of MISA Regulations for Direct Industrial Dischargers in Ontario", in Proceedings of 1988 Technology Transfer Conference, MOE 1988
- VHB Research and Consulting Inc., "Water Pollution Abatement Technology and Cost Study" (forthcoming), Prepared for MOE, Policy and Planning Branch

BACKGROUND

The Hagersville fire broke out in the early hours of February 12, 1990. Between 13 and 14 million tires burned for seventeen days before the fire was successfully extinguished on February 28, 1990 after remarkable efforts on the part of local, regional and provincial firefighting crews. The immediate concerns of environment officials were to assess and control the effects of air-borne pollutants which had settled on local fields and bodies of surface water and of contaminants seeping through the bedrock into the groundwater feeding local wells. Concurrently, health officials directed attention to the possible immediate health risks for exposed inhabitants and to the long-term safety of the water and local agricultural produce.

During the course of the fire, initial contacts were made between local health agencies (Adult Mental Health Services and Haldimand-Norfolk Regional Health Department) concerning crisis intervention to be offered to people suffering stress as a result of the fire, evacuation and contamination. Subsequent discussions, in conjunction with the development of the joint community-Ministry of Environment Public Liaison Committee, led to the creation of the Hagersville Community Outreach Program (HCOP) to assess the psychological and social impacts of the fire on the population within a three kilometer radius of the fire site.

Shortly before the fire, the Ministry of Environment had funded our McMaster research team to examine psychosocial effects in populations exposed to environmental contaminants. The events at Hagersville prompted a supplementary study designed to examine these effects in the population affected by the fire. In so doing, the McMaster team worked in partnership with the HCOP serving as consultants in various phases of the outreach program.

THE MCMASTER STUDY

The objectives of the McMaster study were:

1. To identify the awareness and prevalence of psychosocial impacts among exposed individuals, social networks and communities.
2. To identify the coping strategies used or intended by individuals and social networks.
3. To examine the effects of locational and socio-demographic factors on awareness, psychosocial impacts and coping strategies.
4. To describe the links between awareness, experience and impacts of exposure to environmental contamination.
5. To examine the role of community context on awareness, psychosocial impacts and coping strategies.
6. To document the goals, origins, composition and patterns of influence of social networks and interest groups.
7. To examine and evaluate the impacts upon, and coping strategies used by, the workers on the fire site, including volunteers and ministry personnel.
8. To examine and evaluate the approaches adopted to communicate and consult with the local community regarding their concerns in the wake of the fire.

This paper addresses objectives 1, 2, 3, 5 and 8. The primary data used for this come from depth interviews with 43 residents from the area directly affected by the fire. The context within which the interview data need to be understood is provided by a community profile of the Hagersville area. The paper is structured in the following way: the socio-economic characteristics of the site enumeration areas (EAs) and the research evidence on stress and rural communities are presented. This is followed by a brief description of the research design and then a synthesis of the accounts provided by the residents.

COMMUNITY PROFILE

A community profile was created to provide (1) a general overview of the population surrounding the fire site and (2) possible baseline information relating to psychosocial impacts and coping mechanisms for environmental stress. The profile was constructed using secondary sources: census data from Statistics Canada for the seven enumeration areas (EAs) proximate to the site.

The area is predominantly rural. The population of the seven EAs is just 2100 located in scattered dwellings and in the small settlements of White Oaks, Nober, Villa Nova and Springvale (Map 1). Relative to the province as a whole, the area has a relatively stable population with a higher proportion of husband-wife families, a higher percentage of children, and a lower level of educational attainment (Table 1). It has a relatively less affluent, blue-collar population, but one in which there is a high level of private property ownership. The sociological literature would characterize such a population as generally conservative and inward-looking.

The rurality of the Hagersville population and its socio-demographic profile have implications for possible responses to stressful events. Several factors imply an enhanced capacity to cope with stressful situations. These include: the stability of the population (Lazarus and Folkman, 1984); the rural context, social structure and lifestyle (Tremblay and Anderson, 1970; Fuller, 1985; Sim, 1988); the conventional family structure (Cobb, 1976; Eyles and Woods, 1983; Hodge and Qadeer, 1983); and, following from the previous characteristics, the potential for well-developed social and community support networks (Bromet et al., 1982; Cebota and Beat, 1985; Hodge and Qadeer, 1983). But rural communities have changed and are changing and, as Hodge and Qadeer (1983) point out, familiarity in small communities does not necessarily lead to the presumption of friendliness, sociability or assistance.

Other dimensions of the socio-demographic structure in the Hagersville population imply greater susceptibility to environmental stress. These include the high percentage of households with children, the relatively low socio-economic status of area residents and the high proportion of home owners. Families in early stages of the life cycle are likely to be sensitive to environmental stress (Levine and Stone, 1986; Richardson et al. 1986). Studies by Dohrenwend et al. (1981), Kessler and Cleary (1980) and Kessler (1982) indicate that those in lower status groups are more likely to develop symptoms of distress. Homeowners are also more likely to be affected by psychosocial impacts than renters (Levine and Stone, 1986).

In summary, when compared with the evidence in the literature, the rural situation and socio-demographic attributes of the Hagersville population are such that a diversity of

reactions to the fire could be expected with different sub-groups experiencing different levels of stress, access to support and resources and therefore capacities to cope. This anticipated diversity of responses implies the need for a research design and methodology capable of capturing a quite complex set of individual and group experiences.

THE STUDY OF ENVIRONMENTAL STRESS AND QUESTIONS OF RESEARCH DESIGN

Conceptual, contextual and practical considerations affected the choice of the research design for the Hagersville study. Conceptually, conventional epidemiologic studies of environmental stress give little attention to the roles of community context and systemic properties such as social support, value-system, health care availability in enhancing or militating against stress (Taylor et al., 1989). Contextually, the community profile recognizes the potential significance of these factors in the Hagersville situation. Further, there are practical constraints on the type of research design that could be adopted. First, the potentially affected population as defined by evacuation zone is quite small, about 1300 to 1400 people (adults and children) in some 300 households. Secondly, given the nature of the event, this population was potentially traumatized with feelings of loss, distress and dislocation. An epidemiologic survey was therefore inappropriate and unfeasible. The entry of the research team into the community had to take full account of what already existed in terms of community and provincial support structures as a result of the fire. It had to be fully aware of the sensitivity of the situation so that the research would not be perceived as being an external intrusion on a local disaster. To these ends, the research process was constructed as a partnership not just between the research team and the MoE as funders but also between the team and the community by working in close collaboration with the PLC and HCOP. The sample for the McMaster study was recruited from the families who received home visits. It was, however, doubly selected, being drawn from these families (n:166) who agreed to a follow-up. We talked to 43 households and their stories form the basis of our account of the impacts of the fire. These 43 do, however, provide a cross-section of people within the evacuation zone, some being upwind of the fire, some in the red zone, some on the neighbouring concession lines and some downwind but further away.

Given these conceptual, contextual and practical considerations, we opted for depth interviewing as the primary research method. Depth interviews, and their containing suite of methods, qualitative techniques, seek to learn about the world in ways which do not rigidly structure the direction of enquiry and learning by using simplifying, acontextual and *a priori* definitions (Jones 1987). A depth interview is a conversation which allows the informant to relate in his/her own terms experiences and attitudes that are relevant to the research problem. It allows the researcher to probe deeply, uncover new clues, open up new dimensions of a problem and secure vivid, inclusive accounts based on personal experience (Burgess, 1982). Conversation flows in directions which the respondents want it to go. The interviewer is, however, armed with a checklist of topics that must be covered in some order and way with all respondents (Appendix 1). All the interviews in the present research were taped and transcribed in full to provide the working documents for interpretative analysis.

THE IMPACTS OF THE HAGERSVILLE TIRE FIRE: PRELIMINARY ANALYSIS OF RESIDENT ACCOUNTS

For many, the short-term effects of the fire, evacuation and their aftermath were uncertainty, confusion, distress, anxiety, inconvenience, a concern over health and a sense of loss. Our research interviews were carried out in May so people had time to reflect on what had happened to them during those 17 days in February. Things had also continued to happen to them and so when they were asked about how they cope(d) and what were (are) their worries and concerns we obtain a complex picture which relates not only to the fire and evacuation but also to the clean-up as well.

Coping requires an information base so people can decide what to do. For most, information came from the mass media. In the main, people thought that television provided the most useful and trustworthy information, probably because of the salience of this particular medium in people's everyday lives. While most of their information came from TV, radio and newspapers, they were often able to compare the written or televised accounts with their own experiences. The reported messages were often found lacking, particularly those in newspapers, the stories in which were sometimes seen as sensationalized, trivialized, acontextual or just plain wrong.

Information also came from particular provincial ministries. Those who farmed or had livestock were particularly impressed with the ways in which the Ministry of Agriculture went about its job of gathering and disseminating information and monitoring the quality of produce leaving farms. This information was believed and certainly lessened anxiety (particularly about livelihood). The same cannot be said for the Ministry of the Environment, which had to deal with all the residents and not just farmers. Further, the issues with which the MoE had to deal were wide-ranging and of immediate import to quality of life. While most residents recognized the difficulty of the work undertaken in terms of site clean-up and soil and water testing, there was a lack of understanding when technical data were presented and a general lack of trust, a theme to which we shall return.

The providing of information is a community-level response which may enhance coping capabilities. Other such responses include existing and created support mechanisms. Most people saw the role of the regional government and their local politicians as at best minimal and at worst non-existent. While provincial politicians were not seen in the area, it may be that the regional government is criticized unfairly in that its officers were active but were not perceived to be regional officials. So there was general praise for the on-line officials, particularly at the response centre in Townsend. Those manning the centre were seen as helpful in giving advice, passing people on to the relevant agency, acting as liaison with other bodies and so on. But the specially created mechanism (the HCOP) to see what help people required, to let them tell their stories, to assist with coping was poorly perceived. The research interviewers had often to probe people's responses about the HCOP. Few seemed to know of its existence, although all of our respondents would have been visited by a HCOP volunteer. Some regarded it as a waste of time and money, being an agency likely to increase rather than decrease stress and anxiety by simply asking if people had any worries. In the residents' eyes, the HCOP was not so much a failure as a non-event, something to be pushed to the back of the mind or that was irrelevant to their needs.

How then did people cope? In sum, they coped by themselves or thought that there was nothing really to cope with. Not surprisingly, the family, both immediate and extended, was used as a major resource when people required accommodation and other forms of assistance. Further, many of the anxieties and uncertainties were played out within the family unit. Husbands, wives, partners and children were reciprocally used as sources of support to militate against stress, to talk through problems and so on. Such intense, stress-related interaction was not always positive. Members of the same family disagreed about how to deal with anxieties, what certain things meant and how the unit should respond. Some existing tensions were exacerbated by having to respond to the fire and the clean-up. These difficulties and intensities were found especially amongst those closest to the fire site.

Others thought that there was little need to cope. Their lives had been disrupted for a few days, but all had returned to 'normal'. Coping thus really meant the continuous and incremental adjustment to changing life circumstances. The fire was only one element in these circumstances. And such adjustments were 'natural'. So once the fire and the worst of the clean-up had been lived through, life had to go on as it had before: work had to be carried out, children looked after, the home tended. There is a hint of fatalism or stoicism in such a response which is in some respects close to the 'rural mentality' discussed in the community profile. This conservatism, particularly one used to dealing with crises, seems well-adapted to coping. Those who were relative newcomers to the area did not always share these responses, but also tended to rely on themselves and their extended families (often in Hamilton) to cope.

We examine next longer-term impacts which have arisen through people having to live with and adjust to the effects of the fire. These relate to financial and livelihood concerns, social and community impacts, health effects and environmental impacts.

Compensation has become a divisive issue in the community. Understandably, the MoE was able to process small claims for out-of-pocket expenses caused by the evacuation and minor damage claims more quickly than major claims. All residents were satisfied with compensation for the evacuation, although it often resulted in uneasy feelings inside the extended family as the evacuees had to demand that their relatives bill them for food and accommodation. Very few people thought that the MoE should compensate them for any stress or anxiety that they suffered during the fire or evacuation and their aftermath. Major claims for damage to homes and goods and for buying out those who feel that they cannot return to their homes have not been processed quickly. There is widespread resentment at the speed of processing. This resentment is exacerbated by the perceived insensitivity with which the MoE rehoused those who cannot go back. They were housed in trailers near Townsend. Some families have spent up to six months in these cramped conditions. They firmly believe that there are vacant Ontario housing dwellings to which they could have been moved.

Part of the negotiations for the compensation package involve valuing the home and lot itself. There have been disagreements on these values, mainly because there are few similar properties in the area (and fewer recent sales) and because of a depressed market. In fact a dominant theme among the respondents whatever their location was worry about the impact of the fire on property values. They felt that few outsiders would be willing to buy in the area and if they were it would be at reduced prices. Many conceded though that the impact on property values would be a more short-term effect. The fire and clean-up

would soon receive no media coverage and would no longer be in people's mind. In the long-term, it was thought property values would not be affected, although much would depend on the efficacy of the clean-up operations.

The farmers were also concerned about marketing their produce, fearful that their wholesalers would refuse to accept goods or livestock that came from the Hagersville area. The Ministry of Agriculture had set up produce testing for which the farmers were extremely grateful. In the longer-term, they felt their livelihoods would be more affected by the vagaries of the market. Those with seasonal crops were more worried as were those with businesses that relied on positive public perception e.g. dog kennels. All those with farming or livestock business were however concerned about water and its quality, whether in terms of accessible potable water or of fencing off creeks and water bodies that may be affected by pollutant run-off.

Few social or community impacts were reported by the 43 households. Indeed one of the main themes to emerge is the isolation of the family unit, which points up a changing rural scene. Few felt that the community as community was affected at all by the fire or evacuation. There was a brief coming together during the fire itself and for the first public meetings, but after that most simply and perhaps understandably wanted to get on with their own lives and get those back to 'normal'. Indeed, it was the potentially divisive dimension of compensation rather than community spirit that was mentioned. Further, respondents would refer to the strains on the family of getting lives back together, especially if they had been evacuated. More likely, especially in areas west of Townline and in White Oaks, people wondered what all the fuss was about especially after the plume had disappeared.

Few were concerned then about the health effects of the event. Few saw their physical or mental well-being affected by the fire. Mental well-being did not emerge as a significant theme, except in the short-term and among those households who would not return to their homes. In fact, physical well-being seemed more likely to arise as an anxiety, particularly for respondents' children over whom there was a vague unease about future diseases. There were also vague but general worries about the health of all if the water supply in the area had been adversely affected by the fire and the clean-up.

The fourth theme refers to environmental impacts. Worries about air quality were short-lived but virtually everyone is concerned about water quality. There is fear about the effects of the toxic run-off from the site. This run-off has mainly been collected at a water-treatment plant adjacent to the site but some polluted water has percolated into the groundwater. There is uncertainty in which direction and at what rate this water and the heavy oils and metals from the melted tires will run. If the process is slow, it may be years before the full consequences are known. The December 1991 deadline for long-term compensation is, therefore, regarded as inappropriate. There is also general dissatisfaction about water quality testing that has been and continues to be carried out by the MoE. The site has been ringed with test wells to monitor for toxins and pollutants, but most are dissatisfied, wanting their own well water to be tested.

While water quality is the dominant long-term impact from the residents' point of view, water-testing may also be used to illustrate their attitudes towards government, which in this final set of comments will be linked to reflections on 'causes' of the fire and accountability. There is a widespread mistrust of government, which most probably emanates from general economic and political life in the region and the province. With

respect to the fire, government is seen as insensitive, uncoordinated, slow and uncaring. Parts of its apparatus are viewed positively (e.g., the response centre, Agriculture's involvement and testing, particular on-line MoE workers and officials), but many hold government in contempt not only for the clean-up difficulties but also for allowing the fire to happen in the first place. In fact, few blame the site owner for the fire. He is primarily seen as a businessman trying to earn a living but constrained by government and court inaction. Some saw him as fulfilling a community need by taking the tires. There is a degree of fatalism in some resident's views on causation. The site was seen as an accident waiting to happen. It was inevitable that something would occur, although it must be added the site did not loom large in people's pre-fire minds. The pile was simply part of the landscape. But it was a pile for which the government is held largely accountable in that its various agencies should have listened to Straza's petitions more attentively, policed him more effectively, ensured speedier court action and used the tire tax monies to set up recycling capacity. The government is held accountable then for the circumstances that allowed the fire to happen, not of course the fire itself. Although with the fire, the government is not completely absolved. There were comments that the Young Offenders Act and the probation service were not tough or efficient enough. The youths, who allegedly started the fire, are seen merely as the literal and metaphorical spark. Many though believe that they were native youth and although some recognize that natives suffer many deprivations, stereotypical, racist explanations were employed. With respect to causation, we again see the fire as a potentially divisive force in the community. But overall in terms of accountability, the government is less highly regarded by those in the Hagersville area than it was before.

PRELIMINARY RESEARCH CONCLUSIONS

Three major sets of themes emerge from this preliminary analysis of the resident interviews: the evacuation and its immediate aftermath (only briefly mentioned in this paper); the coping strategies employed and the role of information in coping; and the impacts of the event (economic, community, health, environmental) and the effects of these on attitudes to government through the notion of accountability.

Most residents were aware of the possible effects of the fire but there was a low prevalence of psychosocial impacts. More important were economic and environmental anxieties (objective 1). Further, there were some locational and length of residence variations in impacts (3). For most, however, community appeared to be relatively unimportant (5), while families were the main resources for coping with the fire and evacuation (2). Even the specially created HCOP was not regarded as important, although for consultation purposes, the response centre was highly regarded (8). It is though possible to suggest that community context, defined in terms of rurality and farming, may have shaped the nature of the responses (5). But the 'invisibility' of the disaster meant that after the fire was put out the perception of risk was quite low and mainly concentrated among those who had lived close to the site.

References

- Bromet, B.J. et al. (1982) Reactions of psychiatric patients to the Three Mile Island accident, Archives of General Psychiatry 39, 725-30.
- Burgess, R. (1982) Field research, Allen and Unwin, London.
- Cebota, N. and K. Beat (1985) Women strengthening the farm community, in Fuller *op.cit.*
- Cobb, S. (1976) Social support as a moderator of life stress, Psychosomatic Medicine 38, 300-14.
- Dohrenwend, B.P. et al. (1981) Stress in the community, Annals New York Academy of Science 159-74.
- Eyles, J. and K.J. Woods (1983) The social geography of medicine and health, St. Martins Press, New York.
- Fuller, A.M. (ed) (1985) Farming and the rural community in Ontario, University of Toronto Press, Toronto.
- Hodge, G.D. and M.A. Qadeer (1983) Towns and villages in Canada, Butterworth, Toronto.
- Jones, S. (1987) Depth interviewing, in R. Walker (ed) Applied qualitative research, Sage, Beverly Hills.
- Kessler, R.C. (1982) A disaggregation of the relationship between socioeconomic status and psychological distress, American Sociological Review 47, 752-64.
- Kessler, R.C. and P.D. Cleary (1980) Social class and psychological distress, American Sociological Review 45, 463-78.
- Lazarus, R. and S. Folkman (1984) Stress, appraisal and coping, Springer, New York.
- Levine, A.G. and R.A. Stone (1986) Threats to people and what they value, in A.H. Lebovits et al. (ed) Advances in environmental psychology vol. 6, Erlbaum, New Jersey.
- Richardson, B. et al. (1986) Explaining the social and psychological impacts of a nuclear power plant accident, Journal of Applied Social Psychology 17, 16-36.
- Sim, A.R. (1988) Land and Community, University of Guelph, Guelph.
- Statistics Canada (1987) Canada census 1986, parts 1 and 2, Stats Canada, Ottawa.
- Statistics Canada (1990) Enumeration area statistics: Haldimand-Norfolk region, Stats Canada, Ottawa.
- Taylor, S.M. et al. (1989) The psychosocial impacts of exposure to environmental contaminants in Ontario, Final Report, McMaster University, Hamilton.
- Tremblay, M.A. and W.J. Anderson (1970) Rural Canada in transition, Agricultural Economics Research Council, Ottawa.

Site Location: Hagersville Tire Fire

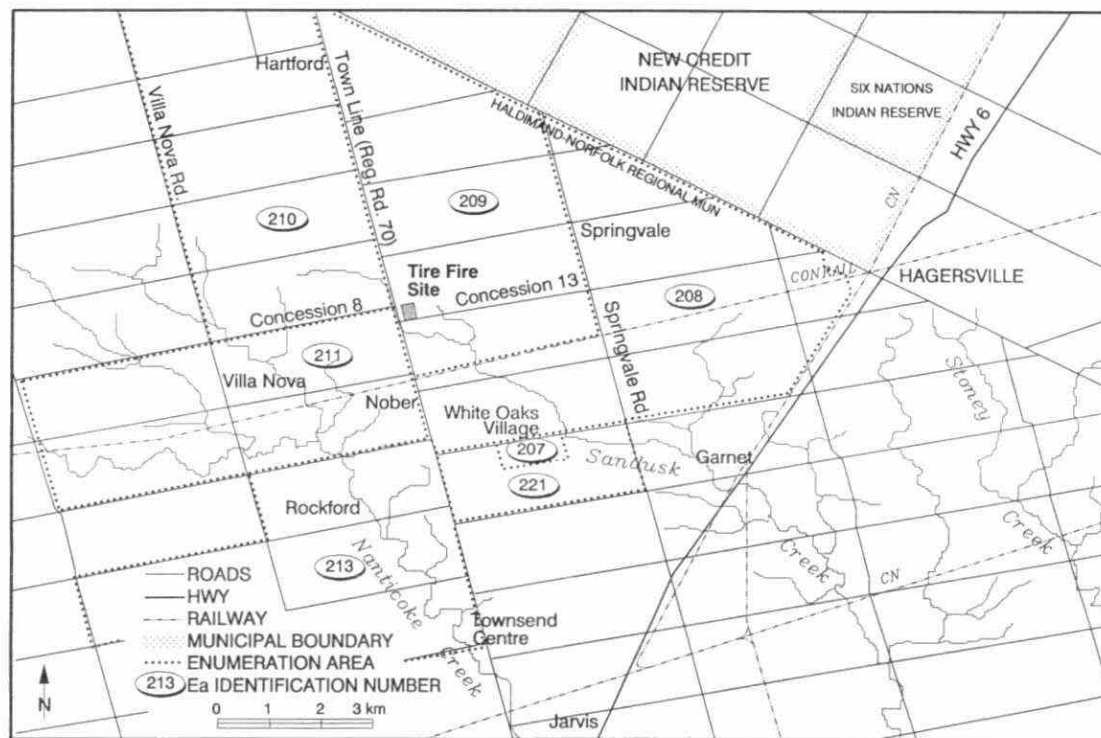


Table 1
Selected Population Characteristics 1986: Ontario, Haldimand-Norfolk, Site EAs

Characteristic	Ontario	H-N	Site EAs
% population change (1981-6)	5.5	0.7	n.a.
% non-movers (1981-6)	55.5	64.9	69.4
% aged 14 and under	20.5	22.5	27.1
average no. of children per census family	1.3	1.3	1.5
% aged 65 and over	10.9	12.6	7.6
% single aged 15 and over	21.1	17.2	13.4
% married	50.8	52.8	49.8
% husband-wife families	88.1	90.9	91.2
% lone parent families	11.9	9.2	8.8
% less than grade 9 education	14.6	15.3	19.9
% university with degree	10.8	3.5	3.8
% primary occupations (male)	2.7	10.9	18.8
% machinery, fabrication, assembly and repair (male)	8.9	10.0	8.7
% service (female)	6.3	5.8	5.2
% sales (female)	4.2	3.4	2.2
% managerial (male)	7.4	4.9	3.5
average household income (\$)	38022	31812	33438
average dwelling value (\$)	104063	71648	88846
% owned dwellings	63.6	74.5	70.9
% single detached house	57.4	83.9	96.1

Sources: Statistics Canada 1987, 1990.

APPENDIX 1: INTERVIEW CHECKLIST

HAGERSVILLE TIRE FIRE

- (1) How did the fire and resulting evacuation affect you?
How did it affect your family? How did it affect your friends?
- (2) Why did all this happen here? Why would it happen here?
- (3) How did you and your family cope?
Have others helped you out, or have you helped others? If so, how?
- PROBE: family
friends
professionals - health, social, others
church
community groups
local and/or provincial government
others
- Are your contacts/ties better or worse as a result?
- (4) What do you think about the job done by the:
- * firefighters
 - * local officials
 - * provincial officials (especially MoE)
 - * media
 - * outreach program
 - * others?
- (5) During the fire and evacuation there must have been alot of information (and rumours) going about. What sources of information about the fire and related events were important?
Were you happier with some sources more than with others? Which ones?
Did you have more trust in certain information sources than in others? Which ones?
- (6) What really worries you now?
- PROBE: own health
health of children
livelihood
property values/image of community
compensation
environmental quality (water, air)
- What do you think will really concern you in three months time?
What about in a year's time?
Do you have any other worries?
- (7) Has the fire and its aftermath changed you?
your family?
your friends?
- For better or for worse?
- (8) Have you lived in this area most or all your life?
If not, when did you move here? Why?
What was good about living here?
What's been difficult in living here?
Have they changed? Will the community be the same again? Why/why not?
- (9) Do you plan to remain in this area?
Is there anything that can be done for you and the community?

VOLUME II

SESSION F

MULTIMEDIA CONTAMINANTS & BIOTECHNOLOGY RESEARCH

VERBAL PRESENTATIONS

Regulating a Multi-Media Contaminant: US EPA's Lead Strategy

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Lead contamination of the industrialized world is ubiquitous and current levels are 1000-fold higher than background, natural levels. Lead contaminates every environmental compartment: air, surface and ground waters, soil and dust, and each compartment is a potential pathway of human exposure. The current literature shows evidence of lead's health effects at lower and lower exposure levels, indeed, at levels previously considered 'safe'.

The US Environmental Protection Agency (EPA) considers lead to be the nation's most toxic multi-media contaminant. It is a significant health problem, primarily because of its impact on infants and children, but also because of its effect on pregnant women and even adult males. EPA is also concerned about the ecological impacts of environmental contamination from lead.

Lead as a Multi-media Pollutant

Lead has hundreds of commercial applications, including as an octane-booster in gasoline; in radiation shields and sheathing for cables; in solder used in plumbing, stained glass and electronics; in pigments for ceramic glazes, paint and newspaper ink; in fine crystal; in pesticides and plant growth regulators; and in hair preparations. Elemental lead is used for water pipes and fishing weights, curtain weights and weights for divers. By volume, most lead is used for automobile batteries.

Each year about 1.2 million metric tons of lead are used in the US and the amount of lead introduced into commerce annually has remained relatively constant for the past 10-20 years, although usage patterns have changed dramatically. The change has occurred primarily because gasoline lead levels have declined by over 98% from the early 1970's to the present, while the number of automobile batteries made and the amount of lead used in them has increased, offsetting the decline in leaded gasoline. Some other sources, such as lead used in solder for food cans, represents a fairly trivial amount of lead by volume, so the recent decline in usage has been almost imperceptible in total lead consumption.

Exposure does not necessarily equate to use. As examples, leaded gasoline was a major use of lead and a major exposure source. Lead in solder in food cans was a trivial use by volume but a significant exposure source. Lead in automobile batteries has been a source of occupational exposure to workers and a major environment pollutant for their families and those in the vicinity, but the use of lead batteries is not a significant exposure source to the general population. Etc.

Blood lead levels in the US have decreased by more than half between the mid 1970's and the late 1980's due to the phasedown of lead in gasoline and reductions in dietary lead. These reductions have had a great effect both on the general population and on populations at-risk of toxicity from specific sources. The principal remaining exposure sources for the general population are drinking water, food, combustion of leaded gasoline, industrial emissions, and soil and dust (interior and exterior) contaminated in the past or present by leaded gasoline and lead-based paint. The principal sources of lead toxicity in children is lead-based paint, followed by drinking water, contaminated soil and dust in urban areas and from the lead industries (smelting, mining and refining), and a host of localized problems such as other occupational exposures (electronics, PVC pipes, munitions, etc.), folk remedies, dietary exposures, hobbies, and even make-up.

At the same time that blood lead levels have been falling in the US, we have been finding that adverse health effects occur at lower exposure levels, indeed, at levels previously thought to be "safe." So the lead problem remains to be "solved".

In addition to the risk of human exposure, lead contamination is also an ecological disaster in much surface and ground water, in huge tracts of land, and appears even in the deepest oceans. Lead is phytotoxic and causes adverse effects in aquatic and terrestrial species. Elemental lead has a very long half-life, and evidence from the Periclean silver mines in Attica and from Roman installations in England suggest that environmental lead pollution does not disappear quickly.

EPA's Regulation of Lead

EPA's regulation of lead began in 1973 when EPA began to restrict the amount of lead used in gasoline. This was done to assure the availability of unleaded gasoline for vehicles with pollution-control devices (catalytic converters) that are fouled by leaded fuel and to reduce exposure to lead. Since then, EPA has further restricted the use of lead in gasoline, and overall combustion of lead in gasoline has been reduced by about 98% in the past 17 years.

In 1978, EPA set a National Ambient Air Quality Standard (NAAQS) for lead, which is 1.5 ug/m³ averaged quarterly. This is still the U.S. ambient air standard, although lead levels in most cities average about 0.1 to 0.4 ug/m³ or 10-20% of the NAAQS. The only places not now attaining the 1978 NAAQS are probably several areas directly around some smelters and battery plants; however, not all stationary sites currently have proximate air monitors. EPA is in the process of re-evaluating the NAAQS and will also likely require the installation of more air monitors in areas at risk of high air lead levels.

The Maximum Contaminant Level (MCL) for lead in drinking water was set in 1975, but EPA merely adopted the standard set by the US Public Health Service in the 1960's. By convention although not by regulation, the MCL is measured in fully

flushed water -- that is, the sample is taken after the water has been running for 2-3 minutes. EPA has proposed to significantly lower the allowable level for lead in US public drinking water. To better protect against exposure to elevated lead levels, it is likely the standard will apply to water that has been sitting in household pipes for 6 hours or more. EPA will probably publish these regulations by the end of 1990.

EPA regulates discharges to surface waters through 2 mechanisms: water quality criteria and industry-specific effluent guidelines. Twenty-three industrial point source categories now regulate the discharge of lead in their waste waters and effluent standards for 2 additional categories (pesticides, and paper and pulp) are being developed; ten new categories are being considered for regulation. Water quality criteria consider the protection of human and aquatic life, recreative uses and aesthetics. Industry-specific effluent guidelines should assure that general water quality standards are not exceeded. The criteria for lead are

	<u>maximum concentration †</u>	<u>average concentration</u>
Freshwater	82 ug/l*	3.2 ug/l*
Salt water	220 ug/l	8.5 ug/l
Human health	50 ug/l**	50 ug/l**

In EPA's hazardous waste programs, wastes are regulated based on their potential to leach lead to ground water. Our waste disposal program, under the authority of the Resource Conservation and Recovery Act (RCRA), requires that solid waste sufficiently contaminated with lead must be disposed of in a permitted hazardous waste disposal facility that is operated so as to protect human health and the environment. The basis for the "tox numbers" used for design, operation, closure and cleanup of hazardous waste facilities are typically Reference Dose values (RfD's) or cancer risk numbers, or in the absence of these numbers, background levels of lead. Whether or not a waste is hazardous is determined by the Toxicity Characteristic Leaching Procedure (TCLP), which has recently replaced the Extraction Procedure (EP) leach test.

Of approximately 1200 Superfund (hazardous waste disposal) sites on the National Priority List, about one-third have lead as a major contaminant. There is no EPA soil-lead standard but the general guideline set by the US Centers for Disease Control of 500-1000 ppm is widely used in clean-ups. Urban soils, which can often

*Fresh water aquatic life criteria for metals are expressed as a function of total hardness (assuming 100 mg/l of CaCO₃).

**These numbers are based on the drinking water standard for lead and will change when a new drinking water regulation is published.

† Maximum concentrations cannot be maintained for more than 96 hours.

reach levels of 500-1000 ppm or even higher in some parts of older cities, may present a complication here.

Finally, lead arsenate and several other inorganic arsenic compounds containing lead are under special review by EPA. The use of pesticides and fruit growth regulators containing lead will probably be voluntarily discontinued; lead arsenate has not been produced since 1985, although in 1989, 10,000 pounds was still available for use in Florida.

Coordinating EPA's Lead Activities

Officially, the development of a multi-media strategy to standardize all aspects of lead contamination, exposure, remediation and effects began in Spring of 1988, with testimony from each of EPA's program offices before EPA's Science Advisory Committee. Its framework was set in the Fall of 1988 when EPA's Office of Research and Development decided to develop a single multi-media research strategy for lead instead of independent programs to support each individual regulatory effort. The overall goals and directions of the agency's many regulatory activities for lead were established this year when EPA's Deputy Administrator called for the development of an EPA-wide Lead Strategy.

Unofficially, of course, coordination on the staff level occurred much earlier because many of the same people support lead research and regulation in the different EPA programs.

Nonetheless, developing a comprehensive lead strategy was not possible without support from the most senior levels of the agency and, of course, targeted resources. EPA, which is perceived by the US Congress as the repository of lead expertise and as an agency capable of successfully tackling large environmental problems, has received \$7.5 million dollars in the past 2-3 years, specifically to address lead problems. In addition, recent legislation and language in our budget appropriations have expanded EPA's authorities and obligations for regulating lead. For instance, the 1987 Lead Contamination Control Act extended to EPA the regulation of water coolers and water fountains, and of water in schools.

EPA's Lead Strategy

EPA's proposed goal for its lead strategy is simple:

Reduce lead exposures to the fullest extent possible, with particular emphasis on the risk to children.

This single goal will be achieved through 2 objectives:

1. Significantly reduce the incidence of blood lead levels over 10 ug/dl in children; and

2. Reduce insofar as feasible the amount of lead introduced into the environment, in order to afford as much protection as possible to both humans and ecosystems.

Achieving the proposed goal is limited by 2 major constraints: authority and resources.

EPA does not presently have regulatory authority regarding most of the sources of either high hazard or general population exposures. Many of the major sources of immediate hazard to children today are a legacy of past uses. These include lead-based paint on the exteriors and interior of buildings; urban soil and dust contaminated by lead from the weathering of lead-based paint; the combustion of leaded gasoline; emissions from a host of industrial sources; and drinking water contaminated primarily by lead leaching from solder used to join copper pipes, faucets (brass and bronze can both contain significant amounts of lead) and flux. Other important sources of lead exposure for the general population include cigarettes, food, occupational exposures, wine and other alcohol, hobbies, ambient air, leaching from ceramics and possibly leaded crystal, and waste disposal practices.

Exposure to in-place lead-based paint, which is probably the largest source of toxicity to children, is not effectively regulated by any Federal agency. The US Department of Housing and Urban Development (HUD) has had responsibility for abating this risk in public housing. However, because of the enormous expense associated with the abatement of this housing as well as policy and programmatic obstacles, HUD has not been able to affect much of this housing. The abatement of private housing is not controlled by any Federal agency. Dietary exposure, which may account for 20-40% of general exposure, is regulated largely by the US Food and Drug Administration. Lead contaminated urban soil may account for another 10-30% of general population exposure and is also likely to be a major source of lead toxicity for US children; no Federal agency has explicit authority to regulate background soil levels. etc.

The costs of abating these exposures are also enormous. As an example, abating one housing unit costs \$3-7,000, and there are probably up to 50 million units requiring abatement. The removal or treatment of lead-contaminated soil probably costs \$1-5,000 for about a half an acre. Many of the 40- 50 million housing units with lead-based paint also have high soil-lead levels, as do areas adjacent to major roadways or industries using lead. Each of these 2 problems is likely to cost about \$10 billion, even if only the most severe parts of the problems are addressed.

A further complication with activities to reduce exposure to lead is that some abatement methods, particularly those related to abating lead-based paint, can actually increase exposure if not carefully and correctly done.

EPA's strategy, therefore, proposes to regulate those exposure sources and pathways under its control, conduct analyses to better assess exposure and to identify

effective abatement technologies, work with other Federal agencies to address sources under their authorities, and mobilize all aspects of the public and private sectors in the effort to abate exposure to lead in the US.

Specifically, EPA's proposed strategy contains the following:

Regulatory activities: --implement a strong pollution prevention program;
--develop soil-lead guidelines;
--re-evaluate the lead NAAQS and develop a plan for bringing all smelters into compliance;
--develop New Source Performance Standards for new facilities;
--publish regulations to reduce lead in drinking water;
--publish regulations for disposal of sewage sludge to minimize lead exposure;
--evaluate the use of lead in all pesticides;
--consider using the Toxic Substances Control Act to restrict new uses of lead and/or phase-out unnecessary or high exposure uses of lead.

Coordination: --within and between EPA programs;
--with other Federal agencies;
--with state and local governments; and
--with the private sector.

Research: --accurately characterize general population and high level lead exposures;
--identify geographic 'hot spots' for lead exposure; and
--develop and transfer efficient and effective lead abatement technology.

Other: --assure the availability of environmentally sound lead recycling.

The Use of Cost-Benefit Analysis

Reducing exposure to lead costs money, in terms of reduced emissions, actual abatement or remediation, switching to more expensive substitutes, and related direct and indirect costs such as required research and development, premature retirement of capital equipment, potential industrial dislocations, etc. On the other hand, continued exposure to lead also costs money, in terms of direct and indirect medical expenses, contamination of surface and ground waters, loss of waterfowl and other aquatic species, damage to plants and the like.

In addition, because of how lead contaminants certain environmental compartments, remediation may actually have unrelated benefits. Two examples are lead contamination of drinking water and the use of leaded gasoline. Lead usually contaminates drinking water by the corrosion of plumbing materials containing lead and the subsequent leaching of lead into the water. The easiest and least expensive way to remediate the problem is to reduce the corrosivity of the

water. Making the water less corrosive reduces all damage from corrosion, resulting in significant cost savings to both consumers and the water utility. Switching to unleaded gasoline provides benefits to vehicle owners in the forms of lower maintenance costs from lead-induced corrosion of exhaust systems and engines, and increased fuel economy. In addition, the use of catalytic converters unfouled by leaded gasoline reduces emissions of conventional air pollutants (hydrocarbons, nitrogen oxides, carbon monoxide).

One way to evaluate a particular action or to compare alternative action is to compare costs and benefits. Costs are generally more easily quantified than benefits and generally relate to common business uncertainties: How long will the machinery last? Will the market grow or contract over the time period considered? What will happen to interest rates? etc.

Benefits are usually more difficult to calculate and, as yet and to my knowledge, no benefit analysis has attempted (or claimed) to estimate all the benefits of a given action. Benefits usually include health and welfare improvements, public goods, decreased ecological and environmental damage, etc.; obviously, these are difficult to even describe qualitatively, let alone to estimate quantitatively. Consequently, they usually underestimate actual benefits.

EPA must decide among many alternatives for reducing lead exposure. This includes evaluating the costs and benefits of different levels for a single action (e.g., different ambient air lead levels) as well as comparing alternative actions (e.g., reducing exposure to lead in drinking water vs lead in paint). EPA often uses cost-benefit analysis where possible in decision-making.

The first major cost-benefit was done to support the 1985 phasedown of lead in gasoline. The methods developed for that analysis were expanded in 1986 and 87 to support the proposal to reduce lead levels in drinking water; the drinking water analysis is being partially redone to support the promulgation of the lead in drinking water regulation. Most recently, EPA has used many of these same methodologies to evaluate the regulation of sewage sludge, an analysis driven largely by concerns over lead.

As examples, Table 1 contains the estimated costs and some of the estimated benefits associated with the 1985 phasedown of lead in gasoline and the drinking water regulation proposed in 1986. For comparison, all costs have been updated to 1989 dollars. As can be seen, while each regulation has significant costs, each is also associated with greater net annual benefits.

Conclusions

Developing workable solutions to the lead problem is technically very complex, and current solutions are extremely expensive, particularly when they involve abatement actions such as removing old paint, soil, or plumbing from

millions of home. And if not carefully done, some abatement efforts can actually increase exposures. Further, lead contamination comes from a variety of sources that are both geographically dispersed and regulated by a wide range of federal and other entities. Finding workable solutions to the array of problems is difficult and must consider both the costs and expected benefits of such actions. Cost-benefit analysis is a tool that can provide guidance to decision-makers.

Table 1: Cost-Benefit Analysis of Two EPA Lead Regulations
(millions 1989 dollars)

	Lead Phasedown* (Gasoline)	Drinking Water Regulation**
Annual Costs	\$ 760	\$ 270
Monetized Annual Health Benefits		
1. <u>Children</u>		
Reduced Medical Costs	\$ 750	\$ 30
Reduced Cognitive Damage	not calculated	\$ 200
2. <u>Adults</u>		
Cardiovascular Effects	\$ 7,300	\$ 340
Other Monetized Annual Benefits		
Vehicle Maintenance Benefits	\$ 1,400	not applicable
Conventional Pollutant Benefits	\$ 280	not applicable
Materials Benefits	not applicable	\$ 610
Total Annual Calculated Benefits	\$ 9,730	\$ 1,180
NET ANNUAL BENEFITS	\$ 8,970	\$ 910

Sources: US EPA, 1985. The Costs and Benefits of Reducing Lead in Gasoline. Office of Policy Analysis. EPA-230-05-85-006.

US EPA, 1986. Reducing Lead in Drinking Water: A Benefit Analysis. Office of Policy Planning and Evaluation. EPA-230-09-86-019.

* Sample year 1986

** Sample year 1988

Application of a Multimedia Risk Assessment Approach to Ontario Soil Contamination Cases.

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Introduction

Regulatory agencies are increasingly relying upon the utilization of risk assessment methodologies as a tool for the effective development of environmental management strategies. In assessing environmental health risks, whether in a site-specific or general population context, it is increasingly recognized that an integrated assessment of exposure from multiple routes is necessary to understand the total risk to the target organisms, as well as the contributory risk posed by the media in question. At the Ontario Ministry of the Environment (MOE), multimedia risk assessment is currently being applied to a number of problems. The following paper describes such an approach as applied to the question of human health implications posed by metal contamination of soils at various Ontario sites. A specific case of copper contamination is described for illustrative purposes.

Elevated levels of copper were found in 1988-89 soil samples collected by the Ministry of the Environment on residential and publicly accessible properties adjacent to Burnstein Castings, a small foundry located in a residential neighbourhood of St. Catharines (MOE, 1990). Residential housing and a public school are located directly adjacent to the site. Quantitative risk assessment was undertaken to consider the question of whether exposure to the reported concentrations of copper in soil might pose a potential health risk to community residents.

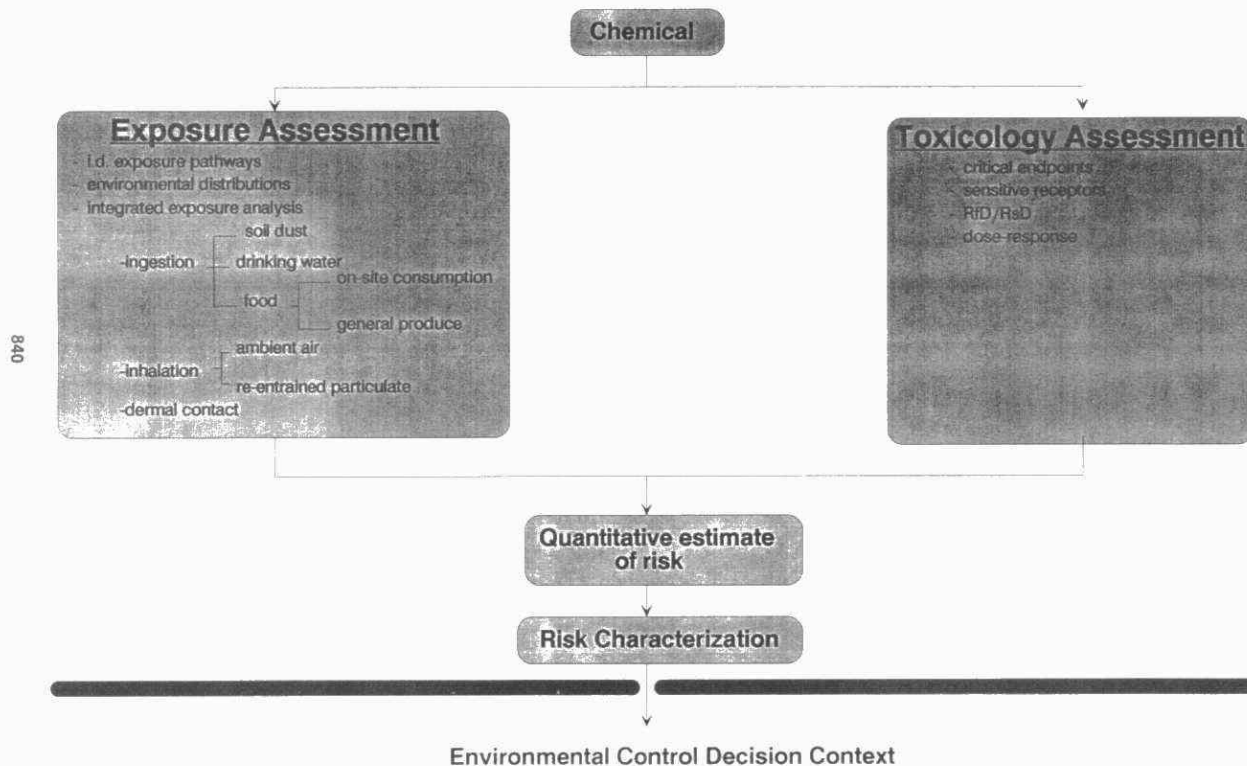
The general approach is based upon conventional models of risk assessment (see Figure 1). The exercise consists primarily of three components: 1.) a review of the known toxicological properties and human health effects of copper; 2.) development of estimates of potential exposures via multiple exposure pathways for adults and young children; and 3.) a characterization of risks from estimated exposures when compared to current exposure limits for copper.

The relative contribution of soil/dust ingestion to total copper exposure is assessed against a simplistic analysis of intake from other pathways (food, air and drinking water), which are modelled utilizing available monitoring data and various human intake assumptions for each media. Average exposures for each pathway are then integrated to provide an estimate of possible total copper intake for individuals in the area. A worst case scenario for soil/dust ingestion and the question of consumption of homegrown produce are also considered.

In characterization of risks, the calculated intakes for copper are compared against existing exposure limits of which there are basically two types: 1.) maximum acceptable daily intakes; and 2.) recommended daily intakes based on minimal nutritional requirements. Based upon this analysis, the copper levels in soil in this community are estimated to result in exposures which are below currently recommended maximum acceptable health limits.

FIGURE 1:

RISK ASSESSMENT FRAMEWORK



Toxicological Assessment of Copper

The biology of copper has previously been the subject of a number of more comprehensive reviews (NAS, 1977, 1980; Stokinger, 1980; WHO, 1984; USEPA, 1985) and the more salient characteristics are summarized here. Copper is considered to be an essential element in the diet of humans for proper nutrition, and it is widely distributed in the body. It is involved in a variety of essential bodily processes including erythrocyte formation, the release of tissue iron and the development of bone, connective tissue and the central nervous system. In addition, Cu is necessary for the proper functioning of many enzyme systems and is associated with certain elements of blood.

Animal experiments indicate that deficiencies of copper are associated with anemia, depigmentation, depressed growth, bone dystrophies and gastrointestinal disorders.

Copper is absorbed from the lungs or gastrointestinal tract following exposure. It has the highest bodily accumulations in the brain, kidney, heart liver and pancreas. Copper appears to be excreted in the feces and at a constant rate by the kidneys. Excess Cu can be eliminated in feces with little change in the rate of elimination from the kidneys.

Although not thoroughly understood, homeostatic mechanisms in normal humans provide a balance between copper intake and elimination. It is known that serum copper levels may vary widely depending on age, sex, hormonal and nutritional status. The homeostatic mechanisms prevent toxicity from the range of normal variations in copper.

Copper is rarely systemically toxic when ingested unless very high amounts are absorbed. Acute poisoning via oral ingestion of Cu is rare due to the powerful emetic action of this metal. However, in instances of large oral exposures, effects such as mucosal irritation, capillary damage, hepatic and renal injury and central nervous system irritation have been reported. Severe gastrointestinal irritation is also associated with large single doses of Cu. Application of concentrated copper salts on the skin has led to papulovesicular eczema and other symptoms, reflecting the corrosive nature of the salts.

Airborne exposures to copper have occurred in the occupational setting. Pulmonary exposures have been observed to result in irritation of the respiratory tract, nausea and metal-fume fever. In some cases, discoloration of the skin and hair has been observed.

The scientific literature is replete with studies regarding the nutritional essentiality of copper, but copper toxicity from chronic exposure has not been well investigated. There are no data indicating that human exposure to copper results in chronic toxic effects. Diets containing up to 5.8 mg of Cu/day have produced no noticeable effects in humans. Long-term inhalation of copper fumes and fine aerosols may result in metal-fume fever. Wilson's disease (hereditary hepatolenticular degeneration), a rare inborn error of metabolism, appears to be the only manifested form of chronic copper toxicity by ingestion in humans. This is a condition characterized by bodily retention of high levels of copper, accumulating in brain, liver and kidney. Another group at increased risk from chronic high level ingestion are individuals with glucose-6-phosphate deficiencies.

There is no evidence that any copper compounds are carcinogenic. The International Agency for research on Cancer has not evaluated copper or copper compounds for carcinogenicity. Copper is classified by the U.S. EPA in the Group D, inadequate data in humans and animals.

Existing Standards and Recommended Limits for Copper

The review of the potential human health implications of copper levels in soils reported in the Phytotoxicology Assessment Surveys stem from observations of levels which exceed the MOE Upper Limit of Normal (ULN) urban guideline for copper in soil of 100 ppm. As indicated in the report, this guideline is based upon a statistical consideration of available analytical data and is not based upon health considerations. The ULN guideline itself therefore provides no comparative health risk benchmark against which to evaluate the elevated soil copper levels. It is therefore useful to consider existing guidelines for copper from other agencies. In the case of copper there are basically two types of limits to consider; 1.) Recommended daily intakes which are based on a minimum nutritional requirement and 2.) Maximum permissible intakes.

1. Recommended Daily Intakes

For children, a World Health Organization recommended daily intake (WHO-RDI) of 0.08 mg/kg body weight (1.2 mg/day for a 15 kg child) is thought to be necessary for proper development.

The National Academy of Sciences (1980) has a recommended daily allowance (RDA) for copper of 2.0 - 3.0 mg/day for adults and 1.5 - 2.5 mg/day for children. The 1980 estimated safe and adequate daily dietary intake (ESADDI) ranges for the adult diet is 2.0 - 3.0 mg/day; the ESADDI ranges for the infant and toddler diets were 0.7 - 1.0 mg/day and 1.0 - 1.5 mg/day respectively.

2. Maximum Permissible Intakes

The joint FAO/WHO Expert Committee on Food Additives has set a limit of 0.5 mg/kg body weight (7.5 mg/day for a child; 35 mg/day for an adult) as an acceptable maximum daily intake for copper.

In the development of a drinking water criteria for copper, the US EPA (1985), has focused on various human studies which suggest that ingestion of between 5.3 and 32 mg of copper/person resulted in gastrointestinal disorders, vomiting, nausea and diarrhea. Because no lasting adverse effects were reported and the symptoms could be the result of local gastrointestinal irritation, the single oral dose of 5.3 mg was considered as a lowest observed adverse effect level (LOAEL). In determining an ADI for copper, a safety factor of 2 was applied to this LOAEL, yielding a value of 2.65 mg/day. This data was also used to calculate a lifetime adjusted ADI, as the acute effects appear to be the effects of concern from exposure to copper.

Human Exposure Assessment

Humans can be exposed to chemicals such as copper from a variety of sources including drinking water, food, ambient air, soil/dusts, occupational settings and consumer products. In order to assess the health significance of copper exposure via a particular route it is necessary to assess total exposure from all routes and compare this against a permissible daily intake. In this case drinking water, air, food and soil/dusts are considered as these are sources common to all individuals. Dermal intakes are not quantified as these are considered not significant. Skin corrosion is not anticipated at the reported environmental levels.

It should be stressed that the exposure exercise in this case is tenuous because of the limited data available on environmental levels in the various media. The approach taken here is to utilize what monitoring data are available and assume that they may be representative. A complete health assessment would require comprehensive information on exposures from all sources and validation of the exposure model would require measurement of appropriate biological indicators. As with any substance, it must also be recognized that individual exposure will vary widely based on many personal choices and several other factors such as geographic location, work, diet, age, sex and health status. Individuals living in the same neighbourhood or household can experience vastly different exposure patterns. The estimates given must be viewed in light of these provisions.

A. Concentrations and Intakes from Individual Sources

1. Soils and Dusts

Exposure to copper in soils can occur via direct ingestion of soil. Soils can also serve as a source of contamination of dusts, as the uppermost layer of soil is subject to re-entrainment by wind and physical disturbance.

The average soil and dust intake for young children (1- 6 years) is estimated to be 80 mg/day. For all other age groups, an intake of 20 mg/day is assumed. From the 1988 - 89 data on copper concentrations in the 0-5 cm layer in soil the following statistics were determined:

- average concentration : 306 ug/g (n=93)
- minimum concentration : 21 ug/g
- maximum concentration : 10000 ug/g

The average was based on 0-5 cm samples only, however the values represent the range on concentrations encountered in all sample points. The maximum concentration represents only one site. The next highest level is 1800 ppm (ug/g).

Using the intake assumption and concentrations the estimated intake of copper for children is:

- average: 24.3 ug/day
- minimum: 1.7 ug/day
- maximum: 800 ug/day

The estimated intake for adults is:

- average: 6.1 ug/day
- minimum: 0.4 ug/day
- maximum: 200 ug/day

In addition to direct ingestion of soil/dusts, soil copper may possibly contribute to total intake through the dietary pathway, as root and leafy vegetables grown in such soil may contain copper residues.

Dermal exposure to copper is not estimated here. Dermal absorption is negligible through intact skin and therefore this pathway is unlikely to be a significant.

2. Drinking Water

The drinking water concentration selected (1.5 ug/L) is the mean of values for treated tap water (Decew Falls effluent) from 5/87 to 5/89 as provided by MOE Welland District Office. Data from consumer taps in the area where soil surveys were conducted were not available. Because this is measured data from the vicinity in question it is utilized in the exposure estimate. It should however also be considered that consumer tap water may contain more copper than the original water supply because of the dissolution of copper from copper piping, which is common in residential housing. The most relevant data of this type comes from a integrated monitoring survey of consumed tapwater in Ontario (MOE, 1989). The average concentration of copper in water over a one week sampling period was 176 ug/L.

3. Air

The air concentration of .15 ug/m³ is the average of data measured from two hi-vol samplers in the vicinity of Burnstein Casting between Nov/86 and May/87. (MOE, 1987).

4. Food

a. General

Dietary copper is generally the primary source for copper exposure. No figures specific to Ontario were found that would provide an estimated intake for this media. Average dietary intakes as determined by the U.S. Food and Drug Administration for 1980 were assumed (Pennington et, 1984 as cited in U.S.EPA, 1985). Use of these figure also assumes no consumption of foods grown on site.

b. Homegrown garden produce

It is not possible to provide a definitive statement as to the potential intake of copper from fruits and vegetables which may be grown in residential gardens in the vicinity of the site. The levels of copper in/on these plants will be a function of both foliar deposition and uptake from soil. The rate and extent of plant uptake of copper is also influenced by the type of produce, length of growing season, and soil characteristics. This type of analysis would therefore require direct sampling data on vegetables from the site.

Modelling of this exposure route also requires assumptions for estimating the consumption of homegrown garden produce. The amounts and types of produce that people might consume from a backyard garden is influenced by the size of the garden, the yields of the crop grown, and the preferences of the receptors.

The actual dose received will also be subject to reductions of concentrations in produce that result during food preparation such as washing, peeling and boiling.

According to the produce module of the AERIS (Aid for Evaluating the Redevelopment of Industrial Sites) Model for exposure, the yields of various types of crops generally range from 0.3 to 2.6 kg/m². For a mixture of crops as might be found in a backyard garden, a yield of 1.4 kg/m² has been recommended, although it is possible to achieve higher yields using special techniques and/or extraordinary effort. The model assumes that a receptors' garden is 30 m² @ a yield of 1.4 kg/m² gives a total of 42 kg, which it is indicated represents 13% of the vegetables and fruits that a one adult and one child would consume in one year. If one assumes a family size of 4, then approximately 7 % of fruits and vegetables would be garden grown.

Nutrition Canada Survey (1972) data for Ontario indicate average daily consumption of fruits, fruit products, and vegetables combined as 372 g/day (26% of total diet) for young children (1-4) and 489 g/day (32 % of total diet) for adult males, which convert to 136 kg/year and 178.5 kg/year. Assuming consumption of these vegetables through the course of the year, average daily consumption of homegrown produce would be 26 g/day for children (1.8 % of diet), 34 g/day for adults (2.2 % of diet).

Vegetable sampling on residential properties in the survey area in 1989 revealed highest copper levels in Swiss chard foliage at 10 ppm dry weight (MOE, 1990). Applying the various produce intake assumptions above and assuming 90% water content for the vegetables, yields an intake estimate of 26 ug/day copper for children and 34 ug/day for adults.

B. Estimated Intakes - Integration of Exposures

The integrated exposure estimates and assumptions employed for typical adults and children are described in Table 1. This exposure model provides crude estimates of possible copper intakes from various media in the vicinity of the Burnstein castings site. The very limited data on water and air concentrations limit the value of these estimates. Also the value assumed for food on the basis of Food and Drug Administration studies of U.S. diets, does not necessarily hold for Ontario. The estimated intakes suggest that dietary copper is by far the largest contribution to total daily intake. The estimated intake from soil/dusts are 0.024 mg/day for young children and 0.006mg/day for adults, based upon the average soil copper concentrations, and represent a relatively minor contribution to total intake. The relative contribution of each pathway to total exposure is shown in Table 2.

The total estimated intakes do not include a contribution from consumption of homegrown produce as the reliability of those "estimates" is considered low. The postulated values do not significantly add to the total intake estimates.

Table 1. Integrated Exposure Estimates for Copper

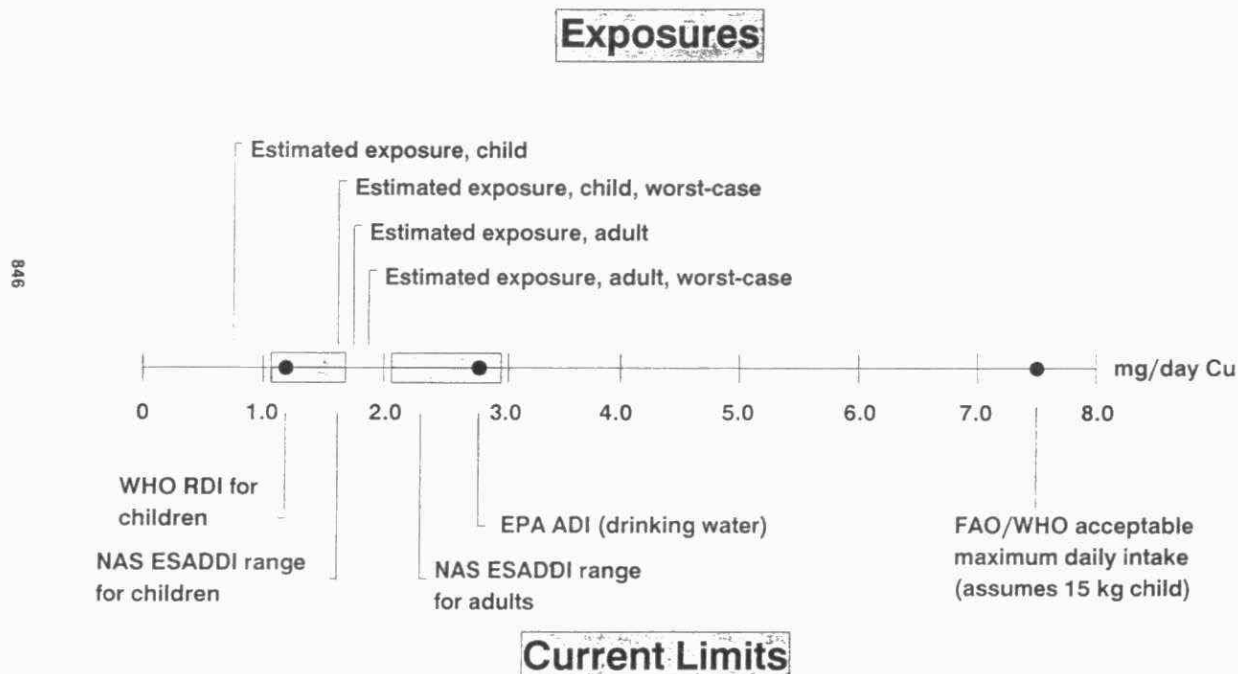
Substrate or Media	Young Children (1-6 years old)	Adults
SOIL/DUSTS		
Average concentration in soil	306 ug/g	306 ug/g
Soil/Dust ingested	80 mg/day	20 mg/day
Estimated Intake via soil	24 ug/day	6 ug/day
AIR		
Concentration of Copper in Air	.15 ug/m ³	.15 ug/m ³
Volume inhaled	5 m ³ /day	22 m ³ /day
Estimated Inhaled copper intake	0.75 ug/day	3.3 ug/day
DRINKING WATER		
Treated tap water concentration	1.5 ug/L	1.5 ug/L
Daily water consumption	0.6L	1.5 L
Estimated Intake of copper from drinking water	0.9 ug/day	2.5 ug/day
FOOD		
Average intake of copper in U.S. toddler and adult male diets in 1980 (USEPA, 1985)	680 ug/day	1600 ug/day
ESTIMATED TOTAL DAILY INTAKE	705.9 ug or .7 mg/day per child	1612 ug or 1.6 mg/day per adult

Table 2. Relative Contributions of Exposure Pathways

Substrate or Media	Child (% Total)	Adult (% Total)
Soil/Dusts	3.5	0.4
Air	0.1	0.2
Drinking water	0.1	0.2
Food	99.2	96.3

FIGURE 2:

RISK CHARACTERIZATION (EXPOSURE AND CURRENT LIMITS FOR Cu)



Risk Characterization

In order to characterize the potential risks associated with copper contamination of soil for this community, the age-specific exposure determinations are compared to current acceptable exposure limits for this substance (see Figure 1). The estimated total exposures (0.7 mg/day/child; 1.6 mg/day/adult), utilizing copper intake from average soil levels, fall below the NAS ESADDI ranges of 1.0 - 1.5 mg/day for children and 2.0 - 3.0 mg/day for adults, the FAO/WHO acceptable maximum daily intake of 0.5 mg/kg/day (7.5 mg/day for a 15 kg child) and the ADI value of 2.65 mg/day suggested by the 1985 EPA Drinking Water Criteria document. As a worst case, if the highest soil copper concentration reported (10,000 ppm) was used in the calculations, estimated intakes of copper via direct ingestion of soil/dusts would be .8 mg/day for children and 0.2 mg/day for adults, yielding total intakes of 1.48 mg and 1.8 mg/day respectively. These worst case values are also below or within the range of acceptable intakes.

Another way to express this information is as a numerical ratio of the total exposure estimates to a reference dose (relative risk ratio, $RRR = \text{exposure} / RfD \text{ or } RSD$). Utilizing the upper limit of the NAS ESADDI ranges for children and adults yields RRR values of 0.46 and .53 respectively. Soil/dust ingestion intakes alone would yield RRR of 1.6×10^{-2} (child) and 2.0×10^{-3} (adult).

The copper levels in soil in this community were estimated to result in exposures which are below currently recommended maximum acceptable health limits. These are not predicted to pose any appreciable risk to area populations based upon the small contribution of soil/dust to total exposure (3.5% , child and less than 1% for adults) and the total multimedia exposure not exceeding current exposure limits.

Other Considerations

The approach outlined above is currently being applied to other Ontario soil monitoring data. The analysis is limited in that it does not model indoor/outdoor exposure or take into account seasonal variability. In the case described this may tend to overestimate exposures. Particular areas of uncertainty are the soil ingestion value utilized, the drinking water concentration and the general food value applied. The estimates given are deterministic and in cases where this simple analysis points to possible risks of concern, some probabilistic calculations would be developed. It is felt that these simplistic exposure estimates facilitate communication and interpretation to decision-makers and lay audiences.

References

- MOE (Ontario Ministry of the Environment) 1987 Particulate Survey of the Burnstein Foundry, St. Catharines.
- MOE (Ontario Ministry of the Environment) 1989. Unpublished data.
- MOE, Ontario Ministry of the Environment (1990) Phytotoxicology assessment surveys Conducted in the Vicinity of Burnstein Castings, St. Catharines -March 1988 through February 1990.ARB-062-90-Phyto.
- NAS (National Academy of Sciences). 1977. Copper: Medicinal; and Biologic Effects of Environmental Pollutants. National Research Council. NAS, Washington.
- NAS (National Academy of Sciences) 1980. Recommended Daily Allowances, 9th rev. ed. Food and Nutrition Board, NAS Washington.
- Nutrition Canada Survey (1972) Food Consumption Patterns Report. National Health and Welfare.
- Pennington, J.A.T., D.B. Wilson, R.F. Newell et al. (1984) Selected Minerals in Foods Survey, 1974- 1982. J. Am. Diet. Assoc. 84(7): 771-780.
- U.S. EPA (1985) Drinking water Criteria Document for Copper. Environmental Criteria and Assessment Office. PB 86-118239
- WHO (World Health Organization). 1984. Guidelines for Drinking Water Quality, Vol I.

A FUGACITY MODEL OF CHEMICAL FATE IN AN UNCERTAIN MULTIMEDIA ENVIRONMENT

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ABSTRACT

A modelling framework is described for estimating prevailing concentrations of chemicals in a regional multimedia environment consisting of four primary compartments, namely air, water, soil and sediment. Each primary compartment is assumed to consist of various proportions of mineral, organic, water, air and biotic phases. A common fugacity applies within, but not between, each primary compartment, although adjustment for non-equilibrium effects such as food chain biomagnification can be included. Steady state fugacities (and hence concentrations and amounts) are calculated from a knowledge of the chemical input rates and the chemical's partitioning and reactivity properties. Intermedia transport rates are expressed in terms of area-specific "transport velocities" which are common to all chemicals and describe processes such as evaporation, deposition and run-off.

The model can be used in conjunction with the "Linear Additivity Principle" to assign "blame" for the prevailing concentrations throughout the system to various sources of chemical.

An uncertainty analysis is included of two types. First, by incrementally adjusting the desired input terms, the sensitivity of the results (e.g. concentrations and amounts) to each input term or parameter can be assessed. This shows which parameters are most critical, i.e. to which parameters the results are most sensitive. Second, by inputting perceived confidence limits to each parameter, and running the program repeatedly with a random but limited variation in each parameter, the overall confidence limits applicable to the results can be assessed.

It is hoped that as more data become available for chemical discharge rates and multimedia concentrations, the model can be more reliably calibrated and used to assess multimedia fate and ecosystem exposure.

INTRODUCTION

There has been a significant recent increase in public concern about environmental contamination by chemicals such as pesticides and solvents. The growing public intolerance to situations in which there are even low concentrations of chemicals in air, food and water is leading to regulatory initiatives to reduce discharge rates to air, water, soil and sewers, and to eliminate the manufacture or import of certain critical persistent and toxic chemicals. Initiatives such as MISA and CAP in Ontario have this thrust.

A major problem in implementing such initiatives is that it is often difficult to identify how source reductions of say 75% removal of a chemical in a water effluent, will eventually translate into a reduction in concentrations in water or fish. Will the reduction also be 75% or will it be only 5%? The reason for this uncertainty is that most chemicals experience multimedia transport, thus for example most of the PCB in Lake Superior is deposited from the atmosphere, thus reductions of PCB quantities in direct discharges to Lake Superior will have little effect on concentrations of PCBs in water or fish. In contrast, discharges of trichloroethylene (TCE) to the aquatic environment generally have little effect on aquatic biota because most of the TCE evaporates to the atmosphere. It is thus necessary to maintain a multi-media perspective on chemical behaviour and build up the capability of deducing likely concentrations in all media as a result of discharges to a specific medium. The beneficial effects of reducing each input can then be explored and the most effective and economic measures can be implemented first. It is believed that the lack of this "cause-effect" link is a major impediment to implementation of practical measures to reduce levels of contamination, in for example, the Great Lakes Basin. When the political system is presented with a clear problem and a clear pragmatic solution it can respond appropriately. The reduction of phosphorus loadings to Lake Erie was an example. But when it has a fuzzy problem such as excessively contaminated fish and no clear set of pragmatic solutions, it fails to respond because it can not justify the cost and inconvenience. The system needs "decision support" in the form of clear statements of cause, effect and benefit, or chemical source and destination.

Regrettably, at present there is no thoroughly validated model of multi-media chemical fate in a regional environment such as Ontario, although some models have been developed and they are continually being improved. It is expected that within ten years a comprehensive multi-media modelling capability will be in place for regions such as Southern Ontario. The principal purpose of this paper is to describe recent developments in this context.

Setting of standards or guidelines should also take place in a multimedia context. The impact of an allowable concentration in one media, for example water, on other media such as air, soil, vegetation, sediment and biota should be considered. The effect on aquatic biota can be approximated from the bioconcentration factor (BCF) and persistence, and is often a determining factor in water guideline or standard setting. However, the amount that will impact air and/or other media is often not considered. For example, in the case of a persistent chemical with a high Henry's constant, the water to air partitioning could result in unacceptable air concentrations.

REGIONAL FUGACITY MODEL

Recently, our group has developed a multi-media model for the Southern Ontario Region exploiting the convenience of the fugacity approach (Mackay and Paterson 1990). For non-volatile chemicals such as metals, a similar "equivalence" approach can be employed (Mackay and Diamond 1989).

Briefly, fugacity f Pa is used as a surrogate for concentration C mol/m³ using the proportionality constant Z which is a function of the chemicals' properties and those of the "dissolving" medium, i.e. C is Zf . When a chemical is present in two phases or media at equilibrium, its fugacity is equal in both phases, just as chemical potential is equal. This formalism facilitates multi-media partitioning calculations by replacing partition coefficients by Z values.

Transport and transformation rates are expressed by D values, such that the rate is D mol/h. D values which have units of mol/Pa.h contain a variety of parameters such as areas, flow rates, mass transfer coefficients, diffusivities and reaction rate constants. Of particular importance are the inter-media transport D values, e.g. for transport from air to water. The overall inter-media D value may contain several contributing parallel processes such as wet and dry deposition and adsorption. Also important are D values for reaction or degradation and advective loss for processes such as removal of chemical from a region by outflow in air or water, or burial in sediment. A full account of this approach can be found in Mackay and Paterson (1982, 1990).

In summary, all equilibrium partitioning characteristics are expressed as Z values (which are thermodynamic quantities), and all transport and transformation processes as D values (which contain Z values) and are kinetic quantities.

MEDIA

As a result of recent work, it has become clear that there is a compelling incentive to reduce the number of media (and hence the number and complexity of the mass balance equations) to a minimum. We believe that four are necessary and generally sufficient, namely air, water, terrestrial soil and aquatic sediment. Although the model treats these four primary compartments as homogeneous media when undertaking multi-media calculations, it is accepted that they consist of several contributing subcompartments such as water, suspended matter and biota. It is assumed that a common fugacity (i.e. equilibrium) prevails for chemical present in the various subcompartments of a medium. This reduces the number of fugacities in the system to four and enables the various subcompartment concentrations to be deduced from the various Z values. An overall or bulk Z value is deduced for each of the four media consisting of an appropriately volume fraction weighted total of the subcompartment values.

The key subcompartment phases are air, water, solid inorganic matter, solid organic matter (i.e. "organic carbon"), vegetable matter and animal matter. Of course, not all of

these phases are present in each medium, but it is convenient to compile a table or matrix of volume fractions in each medium. It is only recently that the importance of terrestrial vegetation as a medium of transport and accumulation has been fully appreciated, so many earlier models have neglected this subcompartment. As a result of research (funded by the Ontario Ministry of Environment) we have been able for the first time to estimate Z values for various vegetation phases and include them in the model. This is important not only because of the potential of vegetation to absorb large quantities of chemical from the atmosphere and soils, but it is a critical vector in calculations of subsequent food chain exposure to domestic animals, humans and wildlife.

This issue of partitioning into vegetation has been under active investigation in our group and has been the subject of several recent reports, notably Paterson and Mackay (1989, 1990). A four compartment (root, stem, inner leaf and cuticle) plant model, illustrated in Figure 1, has been assembled. As in the environmental model, these bulk compartments are considered to consist of subcompartments of varying amounts of air, water and organic matter. Equifugacity is assumed to exist within but not between each bulk compartment. Expressions for Z values have been developed for the various compartments. Transport through the plant is described in terms of D values calculated from transport rates in the transpiration stream or xylem, and in the phloem; diffusivities in the cuticle; and mass transfer coefficients through the stomata. Metabolism in the plant and dilution by growth are also incorporated as D values. The model has been applied illustratively to a soybean plant for several organochlorines. An unsteady state version of the model has also been constructed which incorporates a simple, approximate algebraic solution which estimates the extent of approach to steady state. Validation of the model is in progress.

Table 1 is a matrix of relevant volumes and properties of the various media, the region in question being Southern Ontario.

It transpires that the key Z values used to calculate the various subcompartment and primary media Z values are for the chemical in air, water, octanol (as a surrogate or descriptor for lipids and organic carbon) and for aerosol particles. Biotic Z values are estimated from proportions of water and lipid or octanol values.

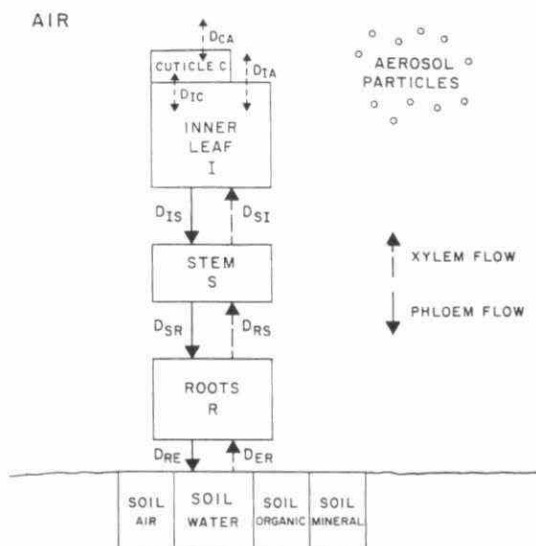


Figure 1. Schematic Illustration of Plant Model.

Table 1. Tentative Media Volumes and Properties.

	Primary Compartment			
	Air (1)	Water (2)	Soil (3)	Sediment (4)
Total Volume m ³	4x10 ¹⁴	4x10 ¹²	1.2x10 ¹⁰	8x10 ⁸
Horizontal area m ²	20x10 ¹⁰	8x10 ¹⁰	12x10 ¹⁰	8x10 ¹⁰
Depth m	2000	50	0.1	0.01
Bulk Density kg/m ³	1.19	1000	1500	1500
Volume fractions				
Air	1	0	0.2	0
Water	0	1.0	0.25	0.3
Inorganic Solids	2x10 ⁻¹¹	4x10 ⁻⁶	0.43	0.65
Organic Solids	0	1x10 ⁻⁶	0.02	0.05
Vegetation	0	1x10 ⁻⁶	0.10	0
Animal	0	1x10 ⁻⁶	0.001	0.001

For the purposes of calculating densities the following subcompartment densities are used: air 1.19, water 1000, inorganic solids 2500, organic solids 1000, vegetation 1000, animal 1000 kg/m³.

Organic carbon content is 56% of organic solids content.

K_{OC} (organic-carbon-water) is 0.41 K_{OW}.

For biotic phases an effective lipid content (equivalent to octanol) of 1% in vegetation and 5% in animals.

Following this approach the volumes and "partitioning capacities" of all media can be deduced for subsequent use in the mass balance calculations.

MASS BALANCES

Mass balances can now be written for each medium including inter-media transport rates, and if the chemical input discharge and advective flow terms are known the equations can be solved to give the prevailing fugacities in each medium. Concentrations and amounts can then be deduced followed by inter-media transport rates. If desired the equations can be written in differential or unsteady state form and solved appropriately to give the time-response of the system.

The overall scheme is illustrated in Figure 2 in which the various D values are identified. Figure 3 is an example of such a calculation showing all transport rates for PCBs at steady state. A complete "chemical behaviour profile" emerges showing the relative importance of each process. An overall environmental residence time or persistence can be deduced.

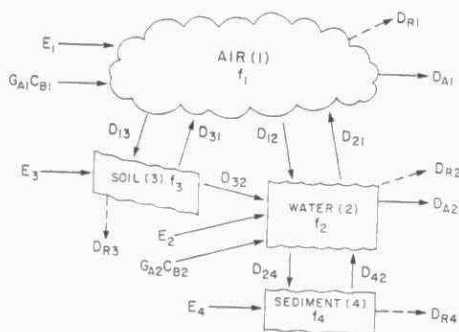


Figure 2. Environmental model illustrating transfer and transformation processes.

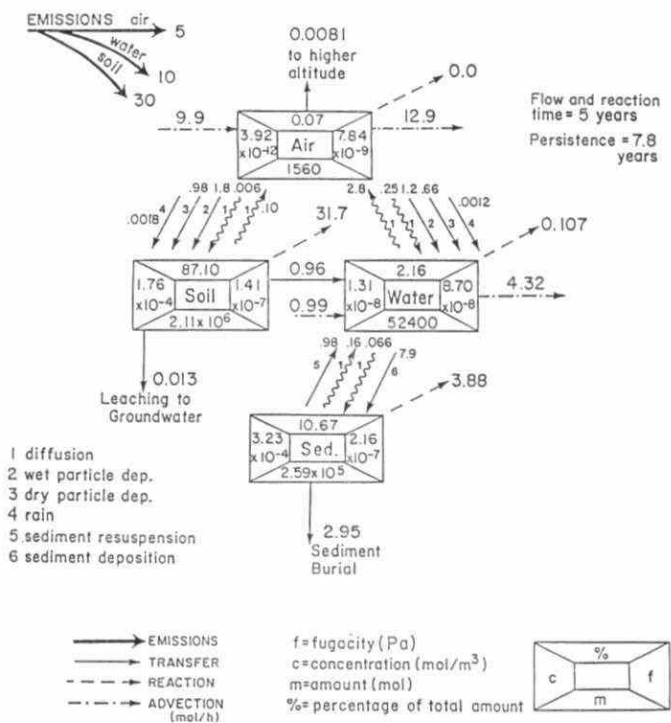


Figure 3. Illustrative mass balance for PCBs.

FOOD CHAIN BIOMAGNIFICATION

A concern with the assumption of equi-fugacity in water is that there is underestimating of concentrations at high trophic levels, because of the biomagnification effect. This can be accommodated by including a simple factor such as 10 to describe this phenomenon, recognizing that this factor is dependent on the chemical's hydrophobicity. As a result of recent work on the biomagnification phenomenon (Clark et al. 1990) we believe that the effect is best described by a factor corresponding to the ratio of organism and food fugacities as calculated from the various physiological parameters such as rates of gill ventilation flow, feeding, growth and metabolism.

This effect is important from the viewpoint of exposure, but because of the small volume of biota, it is insignificant from the viewpoint of the mass balance.

This approach can be applied to biota in the terrestrial and sediment compartments.

MODEL APPLICATIONS

There are three applications of this model which we address in this discussion.

1. Attributing concentrations to sources: the linear additivity principle.

Recently Stiver and Mackay (1989) have discussed the linear additivity principle (LAP), or concept of linear superposition, as it applies to environmental calculations of this type. The principle asserts that if a contaminant's partitioning, transport and transformation processes in a multi-media environment can be expressed exclusively as linear functions of contaminant concentration (as is the case here), then the net contaminant behaviour resulting from multiple discharges in space or time is simply the sum of the behaviour resulting from each discharge individually. The principle is based on the property inherent in a linear system, that individual contaminant discharges behave entirely independently of one another in space and time, i.e. there is no interaction between contaminant discharged

at one location and time, with discharges at other locations and times. At first, this assumption seems counter-intuitive because the rates of transformation and transport depend on total concentrations or gradients in total concentrations. However, as Stiver and Mackay (1989) have demonstrated, fluxes, concentrations and amounts comprise simple linear additions of contributions from individual sources.

The application in this case is to demonstrate how concentrations in the various subcompartments comprise contributions attributable to various sources, i.e. "blame" can be assigned that, for example the concentration in fish is mainly due to discharges to water and is relatively unaffected by discharges to air. This is best illustrated by an example, in this case PCBs.

There are usually five chemical input terms, direct discharges to air, water and soil and advective inflow in air and water. These are listed in Table 2, the relative proportions being obvious. The model is run for each input individually, then for all inputs simultaneously and the fugacities and concentrations noted as in Table 2. It is obvious from the linear nature of the equations that Columns 1 to 5 must add to give Column 6. This is an elementary application of the LAP. It is possible that monitoring data may be available, as in Column 7. If the model equations and parameters and the chemical input rates are correct, any discrepancy between Column 6 and 7 must be attributable to the unsteady state nature of the actual system. For example, in this case the sediments and soil are apparently more contaminated than the steady state values, presumably because of past higher discharge rates. This difference shown in Column 8 is an 'unsteady state' contribution and will (according to the model) decay to zero over a period corresponding to several residence times. It is useful to know how this level of contamination compares with the steady state level because it answers the question "Have we implemented enough controls to ensure long term satisfactory levels in say 10 years, or do we have to do more now? The model can also be used in differential form to identify the response time of the system.

Table 2. Application of the Linear Additivity Principle to the Multimedia Models.

Inputs mol/h	1	2	3	4	5	6	7	8
Discharge to air	5	0	0	0	0	5	-	-
Discharge to water	0	10	0	0	0	10	-	-
discharge to soil	0	0	30	0	0	30	-	-
Advection in air	0	0	0	9.9	0	9.9	-	-
Advection in water	0	0	0	0	0.99	0.99	-	-
Fugacities (nPa)								
Air	2.3	0.90	0.12	4.5	0.09	7.9	-8	-0.2
Water	3.9	63.5	5.8	7.7	6.3	87.2	-90	-3
Soil	3.4	1.4	130	6.8	0.13	141.7	?	?
Sediment	9.6	158	14.3	19.1	15.6	216.6	-400	-184

It is believed that this application of the LAP to multi-media models can be invaluable as a "decision support" mechanism, that is by clearly demonstrating what is accomplished by various remedial activities.

2. Environmental transport velocities.

A difficulty with this and other multi-media models is that there is a large number (possibly 50) of contributing parameters such as volumes, areas, organic carbon contents, flowrates and mass transfer coefficients. The value of each one can be questioned and the sceptical user is rightly concerned that the cumulative effect of having 50 adjustable parameters in a model is that any data can be fitted. Many of the paramaters such as volumes are determined from independent sources, but for many others an element of judgement is necessary in the selection process. In the existing model, a wide variety of environmental data has been exploited to select these values, but there is a possibility that some parameter estimates contain serious error.

An alternative approach would be (in theory) to gather discharge and media concentration data for a number of chemicals, then fit the best values of the 50 parameters to this data set. This is presently impossible because of lack of data and it would probably present severe statistical problems.

Another intermediate, less ambitious approach is to reduce the number of adjustable parameters to a minimum, estimate "typical or reasonable" values, but allow these values to vary within "reasonable" limits and try to fit the available data within these limits. This is a much more constrained and practical task. Accordingly we have devoted considerable effort in recent months to identifying the minimum number of adjustable parameters for describing inter-media process rates.

Examination of the various inter-media transport D values shows that they consist of (or can be rearranged to consist of) a combination of three types of terms. First is the inter-media area $A \text{ m}^2$ which is defined by the dimensions of the environmental system and is available accurately. Second are Z values for the various phases in which transport occurs such as air, water and particles. These are defined by the various partition coefficients, which in turn may be estimated from the relevant physical chemical properties and quantities such as organic carbon contents and Z_v for vegetation. Finally, there are 15 transport parameters, all with dimensions of velocity (m/h) which are multiplied by Z values and areas in various combinations to give the D values, i.e. $D \text{ is } VAZ$. These transport velocities are mass transfer coefficients, flows per unit area or ratios of diffusivity to path length. The entire transport characteristics of the system are thus defined by these 15 "transport velocities" which can be regarded as adjustable or "fittable" constants and which, to a first approximation, are independent of the chemical, although they do contain diffusion rates which are somewhat chemical-dependent. The chemical-to-chemical variability of diffusivity is, however, negligible when compared with the Z value variability.

Table 3 is a list of these "transport velocities" with our current estimates of values. Also given are "confidence limit factors" which essentially correspond to two standard deviations of a lognormal distribution, i.e. in 96% of the cases the value is expected to lie

within a range of values of the parameter multiplied and divided by this factor. It is hoped that as more data becomes available these ranges can be reduced and more definitive values established. Some values such as rain rate are well known, others such as air-stratosphere transfer are relatively unimportant because other parallel processes are faster, thus the problem is not as severe as first appears. Perhaps of most concern is that these are annual average values and thus contain seasonal variations of questionable impact and magnitude. The temperature-averaging problem is particularly difficult.

Table 3. Suggested Transport Velocities and 95% Confidence limit factors (CLF). Values are rounded off to two significant figures.

	m/h	m/year	CLF
air-side air-water MTC	3	26000	3
water-side MTC	0.03	260	4
rain rate	9.7×10^{-5}	0.85	1.5
aerosol deposition	6.0×10^{-10}	5.3×10^{-6}	2
air diffusion in soil	0.015	130	3
water diffusion in soil	5.8×10^{-6}	.051	3
soil boundary layer MTC	1.0	8800	2
water-sediment diffusion	4.7×10^{-4}	4.1	3
sediment deposition	4.6×10^{-8}	0.0004	3
sediment resuspension	1.1×10^{-8}	0.0001	4
soil water run off	3.9×10^{-5}	0.34	2
soil solids run off	2.3×10^{-8}	0.0002	2
sediment burial	3.4×10^{-8}	0.0003	4
air-stratosphere transfer	0.010	90	2
soil-groundwater transfer	3.9×10^{-5}	0.34	2

3. Sensitivity analysis.

Examination of the results of testing this model for a number of chemicals shows that while all 15 velocities influence the fate of a chemical, they do so to very different extents depending on the chemical properties. For example, benzene evaporation is controlled by

the water side mass transfer coefficient and sediment deposition rate is unimportant. For pyrene evaporation is controlled by the air-side coefficient and deposition is important. It follows that different chemicals are differently sensitive to variation in these and other parameters such as vapour pressure or organic carbon content.

To address this issue systematically we have modified the program to adjust (as desired) each parameter incrementally (by 1 %), then recalculate the fate and document the corresponding incremental change in selected output variables. The most sensitive parameters can thus be identified. Interestingly, certain values of chemical and environmental properties are often relatively unimportant (i.e. the results are insensitive), but it is not intuitively obvious which parameters control environmental fate. The corollary to this is that data for a chemical can only be used to determine environmental parameter values such as transport velocities when sufficient sensitivity exists for the parameter to affect the fate significantly. Benzene data can not be used to estimate sediment deposition rates.

From a mathematical viewpoint this process is essentially determination of the partial derivative of the result with respect to the parameter.

MONTE CARLO ANALYSIS

A recurring problem in models of this type is the question: how accurate are the results? The modeller has an obligation to convey an impression of confidence limits. This is most conveniently done by a Monte Carlo Analysis. The approach which we have adopted is to allow all the specified input parameters to vary randomly between defined confidence intervals and calculate a large number of outputs in terms of fugacities or concentrations. These outputs are averaged, distributions established, and limits determined. The outcome is a statement that the output quantity will be an average of say 6 units, but in 95% of the cases it will vary between 4 and 9 units, thus conveying a reliable impression of confidence.

To identify the sources of this variability, the sensitivity results presented earlier can be investigated to determine the most likely candidates. If desired, these sensitivities (or partial derivatives) can be weighted according to the perceived variance in the input parameters to estimate each contribution to the total variance using standard statistical error propagation equations. This enables the "blame" for uncertainty in the results to be assigned to the various input terms. If desired, more effort can then be devoted to obtaining more reliable values of the critical terms to improve the overall accuracy of the prediction.

CONCLUSIONS

In this paper we have reviewed the status of our current attempt to develop multimedia environmental models using the fugacity concept. It is believed that these models will play an increasingly useful role in aiding society to "virtually eliminate" many of these chemicals from our ecosystem. They can be used to document the link between controllable sources and ecosystem concentrations and even exposures and effects, thus identifying and justifying remedial regulatory actions. They can be used to "assign blame" to past and present discharges. It is important, however, to recognize that the models are only approximations of a very complex reality, thus it is essential to establish and convey an impression of reliability or confidence. Current efforts to accomplish this have been described. It is hoped that this will enhance the status of models as "decision support systems" and thus contribute to the purposeful elimination of contamination.

ACKNOWLEDGEMENT

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REFERENCES

- Clark, K.E., Gobas, F.A.P.C., Mackay, D. (1990) Model of organic chemical uptake and clearance by fish from food and water, *Environ. Sci. Technol.* 24, 1203-1213.
- Mackay, D., Diamond, M. (1989) Application of the QWASI (Quantitative Water Air Sediment Interaction) fugacity model to the dynamics of organic and inorganic chemicals in lakes, *Chemosphere* 18, 1343-1365.
- Mackay, D., Paterson, S. (1982) Fugacity Revisted, *Environ. Sci. Technol.* 16, 654-660.
- Mackay, D., Paterson, S. (1990) Evaluating the Multimedia Fate of Organic chemicals: A level III fugacity model, *Environ. Sci. Technol.* (in press).
- Paterson, S., Mackay, D. (1989) Modeling the uptake and distribution of organic chemicals in plants, *in* *Intermedia Pollutant Transport: Modeling and Field Measurement*, Allen, D.T., Cohen, Y., Kaplan, I.R. (eds.), Plenum Pub. Corp., N.Y., pp. 269-282.
- Paterson, S., Mackay, D. (in press, 1990) Current studies on human exposure to chemicals with emphasis on the plant route, *Proc. EPA/ORNL Workshop on Risk Assessment for Municipal Waste Combustion*, Travis, C.C., Hattemer-Frey (eds.), Plenum Press.
- Stiver, W., Mackay, D. (1989) The linear additivity principle in Environmental Modelling: Application to chemical behaviour in soil, *Chemosphere* 19, 1187-1198.

POLLUTANT INTERACTIONS IN MUTAGENICITY TESTING.

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Abstract:

Many agencies test pollutant chemicals as part of their efforts to identify potential biological risks and establish guidelines for use. Natural environments of course contain many chemicals which may interact in unpredictable ways. Thus the actual hazard to plants or animals may be significantly different from that extrapolated from tests of each component alone.

An early model of promutagen interactions in short term assays suggested competition for S9 activation to explain the "less than additive" response when two chemicals were tested together. Viewed from this perspective test systems are multi-enzyme systems and may be amenable to analysis by techniques developed to handle multiple enzyme interactions. In such systems the extent of each pairwise interaction must be assessed. The overall activity is then calculated in a function which aggregates all such interactions.

We have tested nine common airborne pollutants in Ames and Micronucleus assays to develop principles of interaction [benzo(a)pyrene, 7,12-dimethylbenz(a)anthracene, 1-nitropyrene, dibenz(a,h)anthracene, benzo(b)fluoranthene, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, carbon tetrachloride and methylene chloride].

Promutagens when tested together show negative cooperativity. In such cases the surviving activity (within limits) is a linear function of $\log [B]/[A]$ where [B] and [A] are the concentration of promutagens B and A. The actual response is of the form:

$$\text{Response } [A+B] = [\text{Response A} + \text{Response B}] K_{AB} [1 + \log [B]/[A]]$$

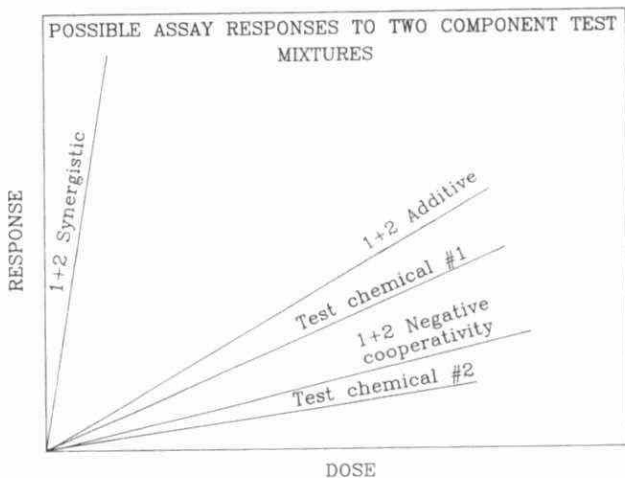
Thus for each pair of interacting chemicals an interaction coefficient K_{AB} can be determined. [Note that such coefficients are assay specific]. Interaction coefficients can then be used to predict the response in more complex mixtures (ie. more components) using a formula of the form:

$$\text{Surviving activity (Risk)} = [\text{Sum of pairwise survivals}] [\text{Substrate availability}]$$

By such an approach we have successfully predicted the activity of several multi component mixtures. Further extrapolation of this technique should allow risk assessment on real, ie. natural, atmospheres.

Introduction

In recent years an extensive literature has accumulated on the effects of individual atmospheric pollutants in various bioassays. In most instances the intention of such assays is to determine what, if any, biohazard is posed by the pollutant. Natural atmospheres of course usually contain several pollutants which may interact in various ways. Thus it would be extremely useful if the data obtained with individual chemicals could be combined in some way to anticipate the effect(s) of complex mixtures. The experience of many researchers however is that the effects of individual chemicals are rarely additive and may range from highly competitive (negative cooperativity) to highly synergistic (positive cooperativity) (Fig. 1). Further, chemicals which are themselves inactive in a particular assay may influence the assay response to another chemical. Thus the prediction of assay response due to mixtures has been elusive.



Our approach derives from a paper (1) in which negative cooperativity was assumed to be due to competition for S9, the enzymatic activating system. If the author's interpretation is correct then such systems are really multi-enzyme systems and the resulting kinetics should be amenable to analysis by the same techniques used for multi-enzyme systems (2). We have tested this approach using nine atmospheric pollutants in two bioassay systems and believe the technique can be used to anticipate the biological response to mixtures of different compositions.

MATERIALS AND METHODS

Chemicals: All chemicals were obtained from Sigma Chemical Co., Aldrich Chemical Co., Chem Service or CTC organic. In each case the highest purity available was used. S9 (a mixture of arochlor induced enzymes) was obtained from the British Columbia Research Institute.

Bacterial Strains: Histidine auxotrophs of *Salmonella typhimurium* strains TA 98 (frame shift mutant), and TA 100 (substitution deletion strain) were obtained from Professor B. Ames.

Mice: B6C3F₁ male mice, were purchased from Harlan Sprague Dawley Inc. The mice were used at 8-9 weeks of age.

Ames' Salmonella assay: The procedure described by Maron and Ames (3) was followed. The "Plate incorporation test" was used for mutagenicity testing. All the mutagens were tested with and without S9. If the solvent control value was within normal range, a test chemical or mixture that produced a positive dose response over three concentrations, with the highest increase equal to at least twice the solvent control value for TA 98 and TA 100, was considered mutagenic.

In vivo bone marrow micronucleus assay: This assay measures chromosomal breakage in bone marrow cells. The Assay procedure used was that of Heddle and Salamone (4) which is a modification of the original procedure of Schmid (5)

Results:Individual Chemicals

The assay responses to each of the nine test chemicals are shown in Table 1.

Table 1**MUTAGENICITY OF INDIVIDUAL TEST CHEMICALS**

Chemical	Ames Assay			Action	MN Assay
	S9	TA 98	TA 100		
1 Nitropyrene	-	+	+	Direct Mutagen	-
DMBA	+	+	+	Promutagen	+
BaP	+	+	+	Promutagen	+
Dibenz(a,h) anthracene	+	+	+	Pormutagen	+
Benzo(b) fluoranthene	+	-	+	Promutagen	+
1,1,1-tri-chloroethane	+	-	-	Non mutagen	+
1,1,2,2-tetra chloroethane	+	-	-	Non mutagen	-
Carbon tetrachloride	+	-	-	Non mutagen	-
Methylene chloride	-	+	+	Direct Mutagen	-

In the Ames Assay 1-Nitropyrene and Methylene chloride are direct acting mutagens while the remaining compounds are promutagens (S9 requiring) or non-mutagenic. In the micronucleus assay all of the promutagens (in the Ames Assay) are mutagenic as is 1,1,1-trichloroethane while neither of the directed acting mutagens (Ames Assay) is mutagenic.

Chemical Combinations:

A variety of pairwise combinations were tested in both assay systems and the data are shown in Tables 2 (Ames Assay) and 3 (Micronucleus Assay).

Table 2
MUTAGENICITY OF CHEMICAL COMBINATIONS
Ames Assay

Chemicals	Assay Response		
	S9	TA 98	TA 100
1NP + DMBA	+	S	S
1NP + BaP	+	S	S
DMBA + BaP	+	NC	NC
BaP + Dibenzo (a,h) anthracene	+	NC	NC
Dibenzo (a,b) anthracene + Benzo (b) fluoranthene	+	NC	NC
Dibenzo (a,h) anthracene + 1,1,1 trichloroethane	+	NC	NC
Benzo (b) fluoranthene + 1,1,1 trichloroethane	+	NM	NM
1,1,2,2 tetrachloroethane + methylene chloride	+	NC	NC
Carbon tetrachloride + methylene chloride	+	NC	NC

S = Synergistic (greater than additive) Response
 NC = Negative Cooperativity (less than additive)
 NM = Non Mutagenic

Table 3
MUTAGENICITY OF CHEMICAL COMBINATIONS

Micronucleus Assay

Chemicals	Assay Response
INP + DMBA	Negative Cooperativity
INP + BaP	Negative Cooperativity
DMBA + BaP	Negative Cooperativity
DMBA + DBA	Negative Cooperativity
BaP + Dibenzo (a,h) anthracene	Negative Cooperativity
Dibenzo (a,h) anthracene + Benzo (b) fluoranthene	Negative Cooperativity
Benzo (b) fluoranthene + 1,1,1 trichloroethane	Non-Mutagenic
1,1,1 trichloroethane + 1,1,2,2 tetrachloroethane	Non-Mutagenic
Carbon tetrachloride + methylene chloride	Non-Mutagenic

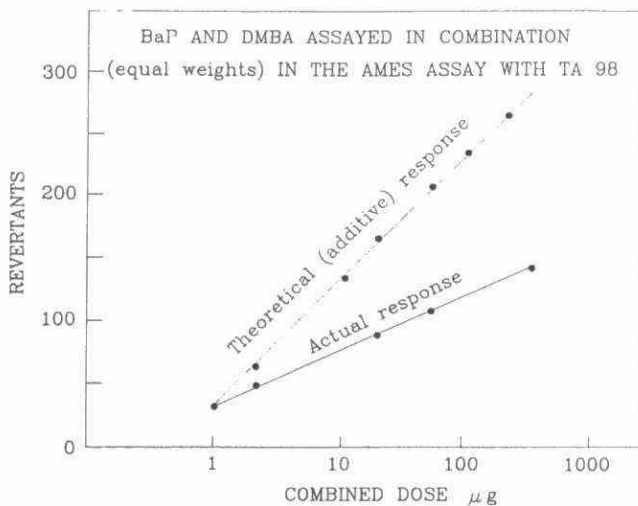
In the Ames Assay combinations involving INP (a direct acting mutagen) give a synergistic response. All other responses show negative cooperativity. In the case of Benzo(a)fluoranthene plus 1,1,1-trichloroethane the mutagenicity due to the former is essentially lost when combined with non-mutagenic 1,1,1-trichloroethane.

In the Micronucleus Assay all combinations were either non-mutagenic or showed negative cooperativity.

For further study of pairwise interactions we chose BaP and DMBA in the Ames Assay.

Benzo(a)pyrene and 7,12 Dimethylbenzo(a)anthracene combined.

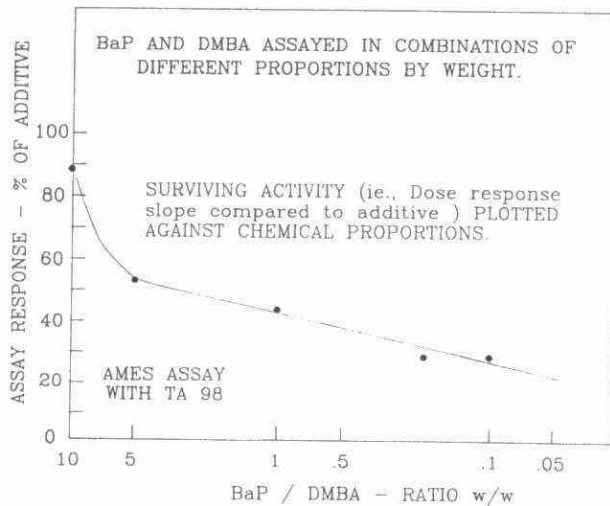
BaP and DMBA are both promutagens which, in the presence of S9, give positive responses in the Ames Assay with TA98. Standard dose response curves can be prepared for each and the anticipated response for any dose calculated. When the chemicals are tested together (with surplus S9) an additive (theoretical) response can be calculated and compared to the actual response. An example is given below.



7

BaP and DMBA combined in different proportions

Figure 2 shows the actual response, compared to an additive (theoretical) response, seen in the Ames assay when BaP and DMBA are added in equal amounts (w/w). This experiment was repeated with differing proportions of the two chemicals and the slope of the actual response compared with the theoretical in each case. The results obtained are shown below (Figure 3).



The addition of DMBA even well below its threshold for activity markedly inhibits the production of revertants. When the proportion of DMBA is 1/10 that of BaP or less, the actual response closely approximates the theoretical. As DMBA is increased however the response (slope of dose response curve) falls dramatically and from $DMBA/BaP = .2$ onward there is a linear relationship between the assay response and the $\log_{10} BaP/DMBA$.

PAIRWISE INTERACTIONS

The preceding figure shows that the two promutagens BaP and DMBA when tested together in the Ames Assay interact to give a predictable response. In this case the theoretical response (ie. additive) is reduced by a factor proportional to the relative concentrations of the two chemicals tested. The actual response can apparently be represented by a formula such as:

Response (A+B) = {Response [A] + Response [B]} K_{AB} (1+log B/A)
When B = A, 1 + log B/A \rightarrow 1. then K_{AB} is the fractional activity remaining.

A similar relationship appears to apply to all pairs of promutagens tested when the chemicals are present in relative concentrations of approximately 1:10 to 10:1. At concentration extremes (ie. > 100:1) K increases towards the value of 1 ie. the response of a single chemical.

For each Promutagen pair an interaction constant K_{AB} can be determined which is assay specific.

Chemical Pair	K_{AB}	
	Ames	MN
BAP + DMBA	.46	.29
DMBA + DBA	NT	.12
DBA + BF	.90	.35
DBA + 1,1,1 trichloroethane	.27	.26
BaP + DBA	.57	.20
BF + 1,1,1 trichloroethane	NM	.52

Complex Mixtures

Natural atmospheres contain many chemicals with varying proportions of each. An obvious question therefore is whether pairwise interactions can be used to predict the biological response to more complex mixtures. To begin to answer this we have tested a three component mixture of BaP, DMBA and DBA (7.5/1.5/1.0. w/w/w) in the micronucleus assay. The K_{AB} 's in this case are 0.29(BaP+DMBA), 0.12(DMBA+DBA) and 0.20(BaP+DBA) and the surviving activities if each pairwise

combination was tested individually would be $KAB[1 + \log B/A]$ i.e. 49%, 13% and 37% respectively.

Addition of the individual pairwise survivals would of course give a higher net surviving activity than would be expected since it does not correct for the "competition" between individual pairs for free molecules in multi-component mixtures.

ie. Net Survival = [Pairwise Survivals] [Correlation
for availability]

Availability should be calculated on a molar rather than weight basis. But if as a first approximation

$$\text{Availability} = \frac{C_i}{C_i - j}$$

where C_i is the overall concentration of each component and $C_i - j$ is the difference in concentration between components i.e. free component.

Then for BaP/DMBA/DBA Surviving Activity would be predicted to be:

$$\frac{[49+13+37]}{[11.5]} = 86\%$$

The actual survival was 86%.

Observations and Conclusions

If assay variables, other than the concentrations of test chemicals, are carefully controlled, the interactions between pairs of chemicals in both Ames and Micronucleus assays is reproducible and predictable. Some features of such interactions include:

- 1) In cases where promutagens interact, the most common response is negative cooperativity;
- 2) The interaction between such promutagens depends on their relative proportions and can be predicted mathematically;
- 3) Non-mutagens may interact with promutagens in a manner similar to another promutagen i.e. modelling of mixtures must include the contribution (interactions) of non-mutagens;
- 4) In the absence of S9 some promutagens will still inhibit the action of a direct acting mutagen in the Ames assay.

These interactions while reproducible in a single assay system demonstrate some of the more general problems of risk assessment of complex mixtures. Such problems include: mutagenicity in one assay but not another, different responses with different bacterial strains (Ames assay), the requirement for S9, etc. In addition to these technical restrictions is the more general problem of extrapolating bacterial, plant or other assay data to anticipate human risk.

In spite of these difficulties risk assessment involving complex mixtures may be more readily achievable than might be predicted. The risk due to individual chemicals can be assessed and their pairwise interactions in an animal test system can be quantitatively measured. The interaction constants thus derived may then be used in the same way as multi-enzyme systems are handled to predict the net effect of several mutagens in mixtures of different proportions.

References

- 1) Salamone, M.F., Heddle, J.A., and Katz, M. Can. J. Genet. Cytol. 21 101 (1979).
- 2) Plowman, K. in Enzyme Kinetics published by McGraw Hill (1972).
- 3) Maron, D.M., and Ames, B.N. Mutat. Res. 113 173 (1983).
- 4) Heddle, J.A. and Salamone, M.F. in Short term tests for carcinogenicity. Eds. H. Stick and R.H.C. Sai. Springer-Verlag N.Y. p. 243 (1981).
- 5) Schmid W. Mutat. Res. 31 9 (1979)

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GENOTOXIC COMPOUNDS ASSOCIATED WITH RESPIRABLE URBAN AIR PARTICULATE. CHEMICAL FRACTIONATION AND BIOASSAY OF COMPLEX MIXTURES.

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INTRODUCTION:

The composition of mixtures of polycyclic aromatic compounds (PAC) found in association with respirable particulate in an urban air environment is dependent on season, atmospheric condition, industrial activity, motor vehicle traffic, residential density and many other variables (1-3). Some of the compounds associated with urban air particulate are toxic or carcinogenic and could have an adverse effect on human health (4,5). Characterization the impact of human activities on environmental health requires the marriage of analytical chemistry and genetic toxicology (the study of chemical or physical activities which pose a mutagenic or carcinogenic risk). Rigorous chemical analyses of organics associated with urban air particulate has provided valuable information about the types and classes of PAC in the environment (6-8). Genotoxicology, on the other hand, has produced new and additional insight into the problems associated with exposures to the complex mixtures of extractable organic compounds from air particulate and the risks such exposures pose to humans (7). While not all known chemical carcinogens are detected by all or, indeed in some cases, any of the STTs, these tests provide the most rapid method of screening for genotoxicity.

Nearly three thousand chemicals have been identified in the earth's atmosphere (6). The chemical analysis of organic extracts of total suspended respirable particulate has been extensively reported (9,10). While initial concerns have been directed at the investigation of the unsubstituted polycyclic aromatic hydrocarbons (PAH), these do not by any means account for all the genotoxic biological activity in environmental samples (11). Complex mixtures extracted from air particulate contain substituted PAH (alkyl, amino, chloro, cyano, hydroxy, oxy or thio groups) as well as heterocyclic derivatives of PAH (7).

The use of biological assays for genotoxic activity in total extractable organic material from urban air particulate has been used to examine the relation between mutagenicity associated with air particulate and a number of factors including seasonal weather patterns, geography, vehicle traffic and industrial development (2). Nishioka *et al.* (12) identified hydroxynitrofluorenone, an hydroxylated and nitrated derivative of pyrene, isomers of hydroxylated nitromethylfluorenone hydroxylated nitro-derivatives of benzene, toluene, naphthalene, and biphenyl in the fractions of a massive air sample which contained significant mutagenic activity.

The objective of this research is to examine polycyclic aromatic hydrocarbons (PAH) and PAH derivatives adsorbed to respirable urban particulate ($<10 \mu\text{m}$) and to assess the health hazard they present. A class-selective chemical fractionation procedure coupled with an analysis by a combination of chromatographic methods and short term tests (SSTs) for genotoxns. We report progress in three areas: (1) chemical characterization of the fractionated material; (2) identification of fractions most active

in bioassays; and (3) correlation of genotoxicity of specific fractions in bacteria with the corresponding activity for DNA adduct production in mammalian cells.

MATERIALS AND METHODS:

Air particulate samples (selected for respirable particulate with aerodynamic diameter $<10\text{ }\mu\text{m}$) were collected for 24h periods using a PM10 sampler (General Metal Works) with flow controller set at $40\text{ ft}^3/\text{min}$ ($1630\text{ m}^3/24\text{h}$). All suspended particulate samples were collected on Teflon/glass fibre filters (Pallflex 8 x 10 inch type TX40H120WW). One sampler was sited at Toronto (Station # 31104) on Bredalbane St., and at two locations in Hamilton: Downtown on the roof of an OME station #29000 at the intersections of Kelly and Elgin Streets, and Westdale (Station # 29118) at the intersection of Main St West and the exit of Highway 403). Typical values for 24h samples are given in Table 1. Actual mean diameter of particulate collected was $0.105\text{ }\mu\text{m}$ (range 0.013 to $0.46\text{ }\mu\text{m}$).

Table 1: COMPARISON OF PM10 RESPIRABLE PARTICULATE BY LOCATION

Average Load: (24h, 40cfm)	Maximum	Minimum
HAMILTON		
Downtown	0.089844g (0.0526) ¹	0.326600 (0.0193)
(Kelly and Elgin)		
Westdale	0.062679g (0.0329)	0.146700 (0.0176)
(Main St. West)		
TORONTO	0.049340g (0.0303)	0.166450 (0.0115)
(Bredalbane)		

¹Standard deviation N = 85

Sample loadings of respirable particulate varied with the site (Table 1). On average Westdale, received seventy percent of the total respirable particulate that was measured at the downtown site on the same days. At the Downtown location where both PM10 and hi-vol units were located, the respirable particulate averaged 62% of the total suspended particulate (0.144223g (.0814) N = 83). Toronto sample values averaged somewhat lower than those from Hamilton (79% of Westdale). An important difference between the values for the two cities was that the Toronto sampler was sited more than 12m above street level, while Hamilton samplers were located at less than 4m.

PARTICULATE EXTRACTION METHODS:

Filters collected for a designated period or atmospheric condition were pooled and Soxhlet extracted successively with dichloromethane (DCM) and methanol (MEOH) for 16h. The organic extract was fractionated according a scheme shown in Figure 1. The organic extract was loaded onto a neutral alumina column and sequentially eluted with

solvents of increasing strength yielding the following fractions: [A1] (hexane), [A2] (benzene), [A3] (CHCl_3 / 1% methanol), [A4] (methanol), [A5] (methanol/water) and [A6] (water). Fractions [A2] and [A3] as well as [A4] and [A5] were pooled to yield fractions [A23] and [A45]. Aliphatics which were a major contaminant in [A23] were removed by chromatography on Sephadex LH20.

Alumina fractions [A23/LH20] and [A45] were subjected to further separation using gradient normal phase and/or gradient reverse phase HPLC. For these tasks a Hewlett Packard 1090 chromatograph equipped with diode array and fluorescence (Kratos) detectors and a HP Chem-Station was used. Preparation of subfractions of alumina fraction [A23LH20] are described. **Normal Phase HPLC Conditions:** 250 x 9.4 mm i.d. 10 μm Whatman Magnum-9 PAC column, maintained at 35°C. **Solvent gradient:** as a percent of dichloromethane (CH_2Cl_2) in hexane at different times; 0% from 0-5 min, 1% at 10 min, 5% at 15 min, 100% at 40 min and then isocratic at 100% CH_2Cl_2 until 50 min. At 50 min a second gradient was initiated from 100% CH_2Cl_2 to 100% absolute ethanol over 10 min then held for 5 min at 100% ethanol. **Flow rate:** 4.2 mL/min. **Reverse Phase HPLC conditions:** Two 250 x 4.6 mm i.d. 10 μm Vydac 201TP104 columns connected in series, maintained at 40°C. **Solvent gradient(linear):** 60% to 100% acetonitrile in water over 30 minutes, then hold at 100% acetonitrile. **Flow rate:** 1.0 mL/min. Details of NPLC or RPLC of fraction [A45] are given in the figure legends.

BACTERIAL ASSAYS:

The *Salmonella typhimurium*/microsome assays for mutagenic activity with or without Araclor 1254 induced rat liver S9 (4%) were performed as described by Maron and Ames (13). Tester strains were supplied by B.N. Ames (TA98) or M. Watanabe (TA1538/DNP[pYG122]).

RESULTS:

Table 2 shows the mutagenic activity found in the crude alumina fractions from the pooled Spring, 1989 filters. Mutagenic activity, expressed as revertants per m^3 air, was determined from dose response curves (five doses, duplicate assays). Virtually all detectable mutagens were divided between the two pooled eluent fractions [A23] and [A45]. All mutagenic activity was recovered after the passage of [A23] through Sephadex LH20 (a step used to remove non-mutagenic aliphatics). Both DIRECT AND INDIRECT acting mutagens (-/+ S9) were about equally divided between these two fractions [A23LH20]: 43.5%; [A45]: 42.7% without S9; [A23LH20]: 49.9%; [A45]: 43% in the presence of S9 microsomal activation.

Fraction [A23LH20] typically contains 50-60% of mutagens detected by the *Salmonella*/microsome assay. The alumina fraction (free of aliphatics) was further fractionated by normal phase chromatography (NPLC) into seven [N] fractions. Results for mutagenicity expressed as revertants per cubic meter are given in Table 3. These values were calculated from linear regression for dose response curves based on five dilutions done in duplicate. Values for a minimum of two doses must exceed 2X background to be considered positive.

TABLE 2: *MUTAGENICITY VALUES FOR ALUMINA FRACTIONS: 1989*

DATE	REVERTANTS PER M ³ OF AIR FRACTION			
	[A1]	[A23/LH20]	[A45]	[A6]
Spring: 1989				
TA98 -S9	0.47	1.58	2.0	0.17
TA98 +S9	0.20	4.50	3.88	0.13

TABLE 3: *[N] FRACTIONS FROM SPRING 1989: RECOVERY OF MUTAGENIC ACTIVITY IN TA98*

FRACTION	rev/m ³ -S9	rev/m ³ +S9
[N1]	0.23 (10.6) ¹	0.26 (6)
[N2]	1.04 (47.9)	2.24 (48.3)
[N3]	0.28 (12.9)	0.32 (7)
[N4]	0.34 (15.7)	0.34 (7)
[N5]	0.18 (8)	0.21 (4.5)
[N6]	0.17 (8)	0.07 (1.5)
[N7]	0.45 (20.7)	1.19 (25.6)
TOTAL ²	2.71	4.64
MUTAGENIC ACTIVITY OF FRACTION [A23LH20] ³ FROM CRUDE ALUMINA):	1.05	3.32
PERCENT RECOVERY: $\Sigma[N1...N7]*100/[A23LH20]$:	258	140

¹ Percent of total activity recovered in the fraction.

² $\Sigma[N1...N7]$ in revertants per cubic meter.

³ Mutagenic activity (expressed as revertants per cubic meter) of total filter equivalents loaded onto column for normal phase chromatography.

An example of the distribution of mutagenic activity in each of these [N] fractions is given in Figure 2. Here, fractions [N1] through [N4] have been further fractionated by reverse phase chromatography (RPLC). Eluant from RPLC run was collected at thirty second intervals and each fraction tested in the *Salmonella* assay. Results are shown for activity with microsomal activation. Compounds in these fractions were identified through computer comparison of the UV spectra of peaks with those in the spectral libraries of PAC's and their derivatives.

Approximately ten percent of the mutagenic activity in [A23LH20] (5% of the total) elutes with [N1] (panel A, Figure 2), the least polar compounds from the NPLC fractionation step. Fraction [N1] of Hamilton air samples typically contain a number of PAH (Figure 3A). Quantities of these compounds vary, but they appear in every [N1] fraction of air extract regardless of wind direction or time of year. Interestingly, [N1] from filters collected in Toronto (which represent lower particulate loadings) contains additional compounds to those of Hamilton. These include triphenylene, benzo(b)naphtho-(2,1-c,d)thiophene, benzo(j)fluoranthene, benzo(a)pyrene, benzo(b)chrysene, benzo(e)pyrene, picene, and anthanthrene (see Figure 3B).

Soxhlet extraction of urban air particulate is preferred over sonication in organic solvent. Quantitative analysis of our extraction protocol using a NBS Standard Reference Material, SRM 1649 (urban dust/organics). The NBS method of extraction was optimized to yield PAH. In the [N1] fraction of the Urban Dust 1649 extract we identified: perylene, fluoranthene, pyrene, triphenylene, benz(a)anthracene, chrysene, benzo(j)fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, picene, and coronene. Quantitative analysis for four compounds detected pyrene, 1.01 g/g, triphenylene, 0.812 g/g, chrysene, 1.13 g/g, and benzo(a)pyrene, 1.09 g/g, out of an original 0.980g sample of particulate. With the exception of pyrene, these values represent a yield of approximately 50% of the values determined by NBS. The values were determined from UV spectra rather than fluorescence which is the more sensitive technique. This, and the fact that the chromatography was not optimized for PAH separation may be an explanation for the variation from NBS values.

Figure 2 shows quite clearly that most of the PAC which show activity in the bioassay system are found in fractions other than [N1] which contains most of the readily identified PAH. Small amounts of individual fractions collected during the RPLC of [N2] were subjected to further analysis. Gas chromatography and gas chromatography/mass spectrometry of specific [R] fractions produced a number of potential identifications. The rise and fall of the total ion current as components exited the column. This was compared to the rise and fall of the mutagenicity in the mutachromatogram. Identities of potential mutagens were ascertained. Analysis of the mass spectral data, resulted in proposal of six structures for nine potential mutagens found in one subfraction [R] of the [N2] fraction and these are presented in see Figure 4. The specific [R] fractions were found to contain ketonic, nitrated, halogenated, and alkylated aromatic hydrocarbons. Two possible structure determinations were a chlorinated quinone and phenanthrene derivative, based of the mass spectral data.

DISCUSSION:

The results presented confirm and extend previous results. Previous reports have examined the influence of ozone, $\text{NO} + \text{NO}_2$ and wind direction on the relative abundance of mutagens detectable by the bacterial assay system. We have used additional, more sensitive strains of bacteria which contained larger amounts of nitroreductase and *N/O*-acetyltransferase which apparently greatly increased the sensitivity of the bioassay system. These strains possess increased ability to metabolise and activate nitro-PAH or PAH derivatives that are acetylated or activated to *N*-acetoxy intermediates. TA98, relative to the other two strains consistently gives the weakest response to a given fraction. Addition of the plasmid pKM101 to these strains has yet again produced a substantial rise in sensitivity of the bioassay (data not shown). This is an indication that a significant portion of the detectable mutagens in atmospheric particulate samples could be nitro-PAH or their derivatives.

The apparent elevated levels of nitro-PAH detected by the bioassay system implicates NO and NO_2 as important actors in the genotoxicity of urban air particulate. Further chemical analysis will clarify which components of the atmospheric emissions provide the greatest concern for human health. The fractions discussed here as well as the more polar [A45] are capable of producing significant numbers of DNA adducts in rabbit tracheal epithelial cells (results not shown). Concentrated research on the identities of the mutagens, the DNA adducts and the mutations they produce in mammalian cells is being carried out in our laboratories.

BIBLIOGRAPHY

- (1) **Arey, J.**, Atkinson, Zielinska and McElroy, P.A. (1989) Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical air pollution episode in Glendora, California. *Environ. Sci. Technol.* **23**, 321-327.
- (2) **Barale, R.**, Zuconi, D., Giorgelli, F., Carducci, A.L., Tonelli, M., and Loprieno, N. (1989) Mutagenicity of airborne particle from a nonindustrial town in Italy. *Environ. Molec. Mutagen.* **13**, 227-233.
- (3) **De Flora, S.**, Bagnasco, M. Izzotti, A., D'Agostini, F., Pala, M. and Valerio, F. (1989) Mutagenicity of polycyclic aromatic hydrocarbon fractions extracted from urban air particulates. *Mutat. Res.* **224**, 305-318.
- (4) **DeMarini, D.M.**, Gallagher, J.E., Houk, V.S. and Simmons, J.E. (1989) Toxicological evaluation of complex industrial wastes: implications for exposure assessment. *Toxicol. Lett.* **49**, 199-214
- (5) **Brown, H.S.** (1988) Management of carcinogenic air emissions: A case study of a power plant. *JAPCA* **38**, 15-58.
- (6) **Graedel, T.E.**, Hawkins, D.T. and Claxton, L.D. (1986) Atmospheric Chemical Compounds Sources, Occurrence, and Bioassay. Academic Press, Inc. N.Y.
- (7) **Vo-Dinh, T.** (1989) Significance of chemical analysis of polycyclic aromatic compounds and related biological systems. In: Chemical Analysis of Polycyclic Aromatic Compounds, ed. Tuan Vo-Dinh, J. Wiley & Sons, Toronto, 1-30.
- (8) **Lane, D.A.** (1989) The fate of polycyclic aromatic compounds in the atmosphere and during sampling. In Chemical analysis of PAC. T. VoDinh ed., J.Wiley and Sons, Toronto; pp. 31-58.
- (9) **Hoff, R.M.** and Chan, K. (1987) Measurement of polycyclic aromatic hydrocarbons in the air along the Niagara River. *Environ. Sci. Technol.* **21**, 556-561.
- (10) **Butler, J.P.**, Kneip, T.J. and Daisey, J.M. (1987) An investigation of interurban variations in the chemical composition and mutagenic activity of airborne particulate organic matter using an integrated chemical class/bioassay system. *Atmospheric Environment* **21**, 883-892.
- (11) **Wornat, M.J.**, Braun, A.G., Hawiger, A., Longwell, J.P. and Sarofim, A.F. (1990) The relationship between mutagenicity and chemical composition of polycyclic aromatic compounds from coal pyrolysis. *Environmental Health Perspectives* **84**, 193-201.
- (12) **Nishioka, M.G.**, Howard, C.C., Contos, D.A., Ball, L.M. and Lewtas, J. (1988) Detection of hydroxylated nitro aromatic and hydroxylated nitro polycyclic aromatic compounds in an ambient air particulate extract using bioassay-directed fractionation. *Environ. Sci. Technol.* **22**, 908-915.
- (13) **Maron, D.M.** and Ames B.N. (1983) Revised methods for the Salmonella mutagenicity test. *Mutation Research* **113**, 173-215.

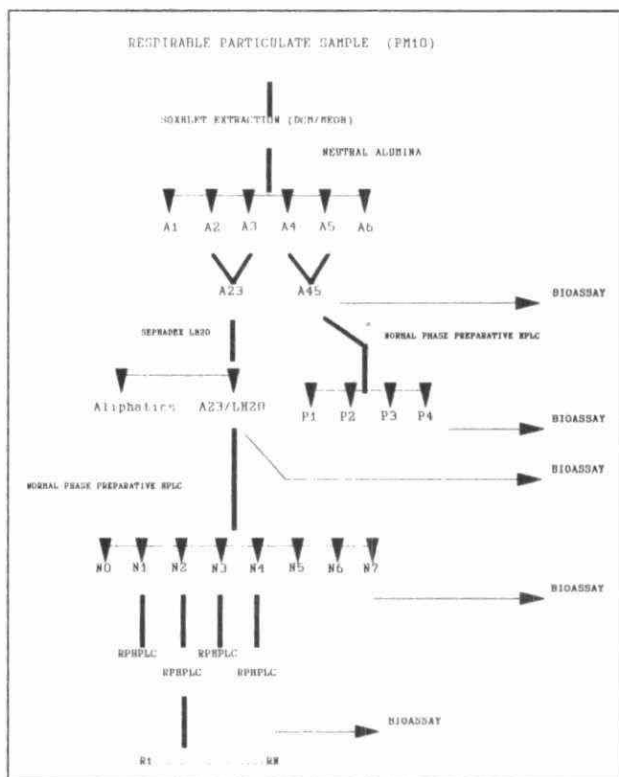


Figure 1: Overall fractionation scheme for organic extract of respirable air particulate.

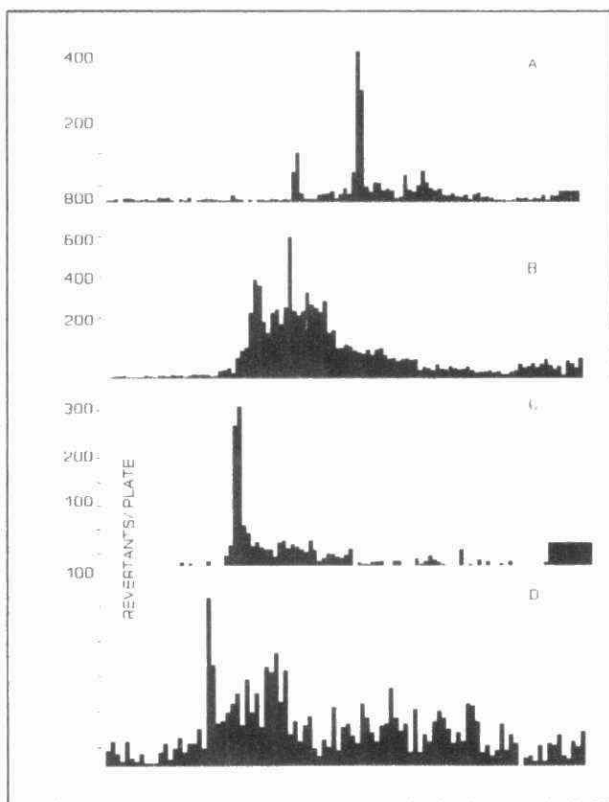


Figure 2: Reverse phase HPLC mutachromatograms of [N] fractions. An example of how mutagenic activity is distributed in [A23/LH20] using *Salmonella* strain TA1538/DNP9(pYG122) with S9 activation.

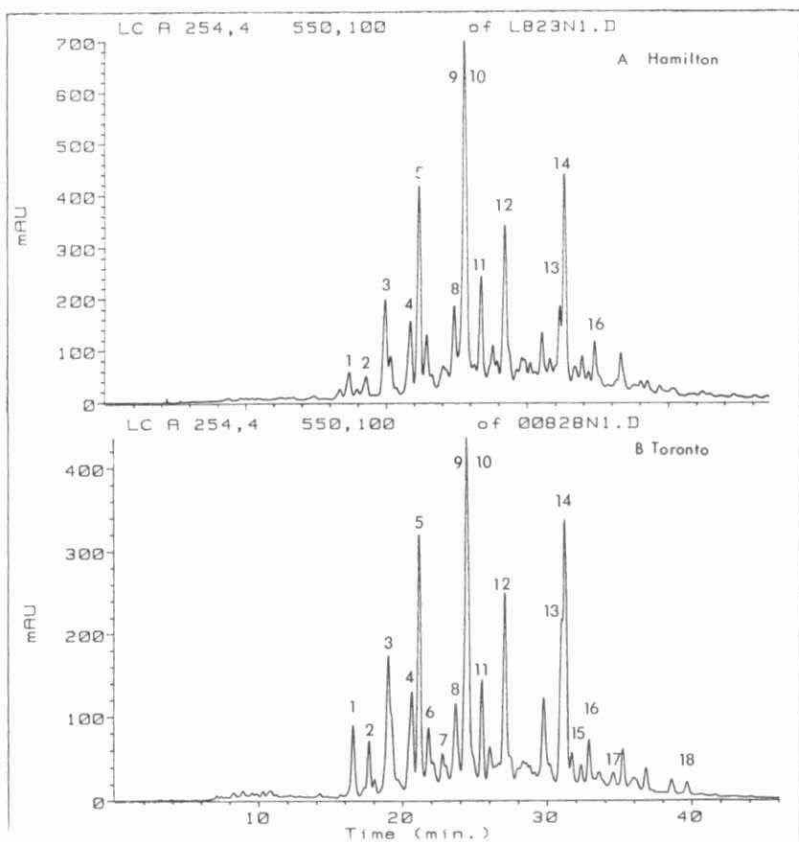
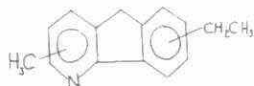
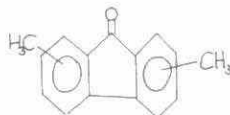


Figure 3: Reverse Phase Chromatography of [N1] fractions from (A) Hamilton air particulate, or (B) Toronto air particulate. The absorbance profiles at 254 nm are shown although spectral information was acquired between 240 and 550nm.

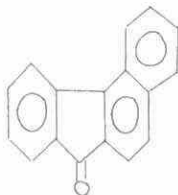
- | | |
|---------------------------------------|------------------------------|
| (1) Fluoranthene | (10) Benzo[b]fluoranthene |
| (2) Pyrene | (11) Benzo[k]fluoranthene |
| (3) Benzo[b]fluorene | (12) Benzo[a]pyrene |
| (4) Benzo[a]anthracene | (13) Benzo[ghi]perylene |
| (5) Chrysene | (14) Indeno[1,2,3,-cd]pyrene |
| (6) Triphenylene | (15) Benzo[b]chrysene |
| (7) Benzo[b]naphtho[2,1-c,d]thiophene | (16) Picene |
| (8) Benzo[j]fluoranthene | (17) Anthanthrene |
| (9) Benzo[e]pyrene | (18) Coronene |



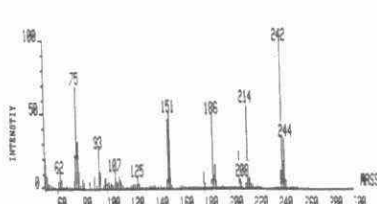
The structure for the compound which eluted at scan number 367 in fraction 19.



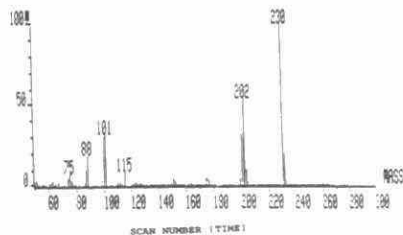
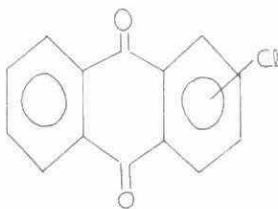
The structure for the compound which eluted at scan number 590 in fraction 19.



The structure for the compound which eluted at scan number 728 in fraction 20.



The mass spectrum for scan number 437 in fraction 20. The below structure is for a compound which may be causing the indirect mutagenic activity.



The mass spectrum for scan number 699 in fraction 20. The structure below is of a possible mutagen which may be causing the indirect mutagenic activity.

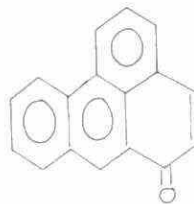


Figure 4: Structures of possible mutagenic compounds isolated from [N2].

Ministry Research Needs in Biotechnology

by

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Introduction

The Ministry of the Environment has only recently become involved in biotechnology, which can be defined as the application living organisms or their products and by-products to provide goods and services. As many applications of biotechnology will involve the introduction of novel organisms directly into the environment, concerns have been raised regarding the risks to human health and the environment which may be associated with such introductions. Regulations are being developed in various jurisdictions to ensure that the risks associated with biotechnology products are assessed prior to their environmental introduction. A major component of these regulations is the development of scientifically founded approaches for assessing the risks in the area of biotechnology. To gain a better understanding of factors which need to be considered when assessing novel organisms prior to their environmental introduction, the Ministry has identified several key issues related to biotechnology risk assessment as potential areas in which to sponsor innovative research. These issues include: the development of detection and monitoring methods, the investigation of gene transfer phenomena, contingency planning, and general microbial ecology.

The Ministry also recognizes that many applications of biotechnology can provide significant social and economic benefits. These can result from reducing our dependence on traditional chemicals and through the development and exploitation of organisms designed to metabolize toxic compounds *in situ*. The Ministry has therefore identified the environmental applications of biotechnology as an additional area in which to sponsor innovative research. For the environmental applications of biotechnology, research is needed in the areas of bioremediation, analytical methodology, and biological alternatives to chemical pest control agents.

Details of the specific research needs in each of these areas are discussed below.

Research Needed

I. Assessing the Environmental Impact of Novel Organisms

The short and long term impact that repeated applications of biotechnology products, especially novel microorganisms, might have on the environment is poorly understood. In order to gain a better understanding of the risks which may

be associated with such introductions, research is needed to understand of the biological relationships in various ecosystems and how they might be affected by the introduction of novel organisms or organisms engineered to carry novel traits.

I A. Detection and Monitoring

- Develop and evaluate sensitive methods for detecting and accurately enumerating populations of microorganisms in terrestrial and aquatic environments.
- Develop improved methods for recovering and analyzing DNA from environmental samples.
- Develop genetic or biochemical markers which can be used to unambiguously identify and quantify populations of novel organisms introduced into the environment.

I B. Contingency Planning

- Develop suitable protocols and methods to deal with accidental spills and releases of biotechnology products containing viable microorganisms.

I C. Gene Transfer

- Investigate and develop methods to accurately determine the degree of genetic transfer which may occur between and among, discrete populations of microorganisms.
- Investigate the environmental and genetic factors which contribute to genetic transfer between, and among, species or strains of microorganisms.

I D. Ecological Effects

- Investigate and identify natural variables which may have an impact on the population dynamics and species diversity in terrestrial or aquatic ecosystems.
- Based on the known factors which influence population dynamics and species diversity in established ecosystems, develop predictive models to estimate the potential environmental impact that novel organisms might have on a particular ecosystem.
- Investigate biological, or physical parameters for use as sensitive end points

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